UNIVERSITY OF HAWAII
APR 4 '56

GEOCHIMICA ET COSMOCHIMICA ACTA

EDITORIAL ADVISORY BOARD

T. BARTH-OSLO N. L. BOWEN-WASHINGTON, D.C. · A. F. BUDDINGTON-PRINCETON, N. J. L. CAPDECOMME-TOULOUSE · E. J. CONWAY-DUBLIN · P. ESKOLA-HELSINKI P. GALLITELLI-MODENA · D. GUIMARÃES-BELO HORIZONTE · A. HADDING-LUND O. HAHN-GÖTTINGEN · H. W. HARVEY-PLYMOUTH · F. HEIDE-JENA · A. HOLMES-EDINBURGH · G. E. HUTCHINSON-NEW HAVEN, CONN. · W. Q. KENNEDY-LEEDS PH. H. KUENEN-GRONINGEN · S. LANDERGREN-STOCKHOLM · F. MACHATSCHKI-VIENNA · B. H. MASON-BLOOMINGTON, IND. · A. MUIR-HARPENDEN · J. ORCEL-PARIS E. RAGUIN-PARIS · K. RANKAMA-HELSINKI · E. REINHARD-BASLE · TH. G. SAHAMA-HELSINKI · C. E. TILLEY-CAMBRIDGE · H. C. UREY-CHICAGO · T. VOGT-TRONDHEIM W. WAHL-HELSINKI · T. WATANABE-TOKYO · F. WHIPPLE-CAMBRIDGE, MASS. R. WILDT-NEW HAVEN, CONN.

EDITORS

L. H. AHRENS
OXFORD

C. W. CORRENS
GÖTTINGEN

E. INGERSON
WASHINGTON

S. R. NOCKOLDS
CAMBRIDGE

F. A. PANETH
MAINZ

L. R. WAGER
OXFORD

F. E. WICKMAN
STOCKHOLM

VOLUME 6 No. 4

NOVEMBER, 1954

PERGAMON PRESS LTD · LONDON & NEW YORK

Geochim. et Cosmochim. Acta

GEOCHIMICA ET COSMOCHIMICA ACTA

EDITORS

DR. L. H. AHRENS, *Department of Geology and Mineralogy, The University, Oxford, England.*

PROF. C. W. CORRENS, *Sedimentpetrographisches Institut der Universität, Lotzestr. 13, Göttingen, British Zone, Germany.*

DR. E. INGERSON, *United States Department of the Interior, U.S. Geological Survey, Washington 25, D.C., U.S.A.*

DR. S. R. NOCKOLDS, *Department of Mineralogy and Petrology, The University, Cambridge, England*

PROF. F. A. PANETH, F.R.S., *Max-Planck-Institut für Chemie, Mainz, Saarstrasse 23, Germany.*

PROF. L. R. WAGER, F.R.S., *Department of Geology and Mineralogy, The University, Oxford, England.*

PROF. F. E. WICKMAN, *Naturhistoriska Riksmuseets, Mineralogiska Avdelning, Stockholm 50, Sweden.*

PERGAMON WAS THE NAME OF A GREEK TOWN IN ASIA MINOR, FAMOUS FOR ONE OF THE GREAT WORKS OF ART, THE ALTAR OF PERGAMON, DEDICATED TO ATHENA.

THE COLOPHON ON THE FRONT COVER IS A REPRODUCTION OF A COIN FOUND AT HERAKLEIA, DATING FROM ABOUT FOUR-HUNDRED B.C., SHOWING THE HEAD OF ATHENA.

VOLUME 6, NO. 4 NOVEMBER, 1954

CONTENTS

PAGE

H. S. YODER and H. P. EUGSTER: Phlogopite synthesis and stability range . . 157

HARMON CRAIG: Geochemical implications of the isotopic composition of carbon in ancient rocks. 186

F. E. SENFTLE, T. A. FARLEY and L. R. STIEFF: A theoretical study of alpha star populations in loaded nuclear emulsions 197

Book review:

"Catalogue of Meteorites" by G. T. PRIOR (Reviewed by F. A. PANETH) 208

Publishing Offices: Pergamon Press Ltd., Maxwell House, Marylebone Road, London, N.W.1 (AMB 3421).

Subscription per volume (including postage) £4 10s. (U.S.A. $12.60).

Distributors: Lange, Maxwell & Springer Ltd., Maxwell House, Marylebone Road, London, N.W.1.

and Pergamon Press Inc., 122 East 55th Street, New York 22, N.Y.

PERGAMON PRESS LTD., MAXWELL HOUSE. MARYLEBONE ROAD, LONDON, N.W.1
PERGAMON PRESS INC., 122 EAST 55TH STREET, NEW YORK 22, N.Y.

Geochimica et Cosmochimica Acta, 1954, Vol. 6, pp. 157 to 185. Pergamon Press Ltd., London

Phlogopite synthesis and stability range

H. S. Yoder and H. P. Eugster
Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C.

(*Received* 21 *June* 1954)

ABSTRACT

A hydroxyl-bearing phlogopite has been synthesized and its upper stability limit determined up to 75,000 psi water vapour pressure. Above the upper stability limit the stable phases are forsterite + leucite + orthorhombic $KAlSiO_4$ + vapour.

At the lowest temperatures investigated the mica grows quickly as randomly stacked one-layer monoclinic phlogopite (1Md). At higher temperatures or with longer runs the mica orders to either a one-layer monoclinic (1M) or a three-layer trigonal (3T) polymorph. It is not possible to distinguish the 1M or the 3T polymorphs by means of powder X-ray diffraction patterns; however, the two-layer monoclinic (2M) mica is easily identified. The small size of the synthetic crystals prohibited identification of their polymorphic form by optical methods or single-crystal studies.

The upper stability range of two natural phlogopites is in accord with that of synthetic phlogopite. The transformation of a natural 2M to a 1M or a 3T was accomplished; however, the stability ranges of the natural phlogopite polymorphs could not be fixed because of the sluggish nature of the transformations and the character of the recrystallization.

The behaviour of phlogopite in igneous rocks high or low in silica is accounted for by the relation of its stability curve to the minimum melting curves of "granite" and "basalt."

The trioctahedral clay micas are identified structurally as 1Md micas. The completely disordered phlogopite produced synthetically and its subsequent ordering well illustrate the observed stages of authigenic growth or, conversely, a weathering of the natural micas.

Introduction

The ubiquitous occurrence of the micas makes them of considerable importance in studies of all rock types—igenous, metamorphic, and sedimentary. Members of the mica group are found under the entire range of geologic conditions: in lavas, granites, marbles, and sediments; in veins and alteration zones; and as weathering products. An investigation of their individual properties and stability conditions was considered, therefore, to be of paramount importance.

The preliminary work leading to the present investigation of the mica group began many years ago at the Geophysical Laboratory and culminated in the completion of a portion of the system K_2O—MgO—Al_2O_3—SiO_2 (Schairer, 1954) and in the studies in the MgO—Al_2O_3—SiO_2—H_2O system (Yoder, 1952b). On this foundation of experimental data and technique, it was deemed timely to tackle the five-component system involving a volatile constituent, K_2O—MgO—Al_2O_3—SiO_2—H_2O, in which the most common micas appear. In addition, with some disregard for the customary systematic approach to complicated mineral groups, exploratory runs were found to be feasible on those micas involving six component oxides.

Those end members of the mica group which are investigated include: phlogopite, annite, eastonite, muscovite, leucophyllite, paragonite, margarite, polylithionite, and many of their fluorine-bearing analogues. The study of their mutual relations and their stabilities relative to those minerals commonly associated with them required data on the following joins: phlogopite—muscovite, phlogopite—eastonite, phlogopite—quartz, phlogopite—annite, muscovite—leucophyllite, muscovite

—quartz, muscovite—clinochlore, muscovite—paragonite, and muscovite—montmorillonite. These experiments were aimed at problems such as determining the nature of the high-silica micas often found in metamorphic rocks, the composition of the mica-like clay minerals which occur in the fine-grained sediments, the chlorite-muscovite reaction marking the biotite isograd, the relation of the breakdown of muscovite to the second sillimanite (or orthoclase) isograd (Heald, 1950, p. 75), the significance of the absence or presence of mica in lavas, and the controls governing the existence of one or two micas in some igneous rocks. In addition to these problems it was necessary to deal with questions of crystal structure arising from the polymorphism of these layered minerals. Many of the above considerations were, of course, dependent on the successful synthesis of the various minerals; and the foremost task was, therefore, the production of the desired phases.

The results of the numerous experiments will be presented in a series of papers, the first of which deals with phlogopite and its related petrological problems.

Previous and related studies

The previous syntheses of phlogopite have been confined mainly to the fluorophlogopites, $KMg_3AlSi_3O_{10}F_2$, with the view toward commerical production. However, Roy (1949, p. 207) reported the growth of hydroxyl-bearing phlogopite under conditions ranging from 400° to 650°C, 10,000 to 1000 pounds per square inch water vapour pressure, and 12 to 100 hours, from natural phlogopite decomposed in the dry way at 1050°C. Although the large laths observed by Roy may be original natural mica unaffected by the heat treatment or simply the hydration of large crystals dehydrated without loss of structure, the appearance of broad mica peaks in the powder X-ray diffraction pattern and the simultaneous disappearance of peaks assigned to the decomposition products are believed by the writers to be sufficient evidence of growth of phlogopite.

The phlogopite composition has also been studied by Roy (1949, p. 205) in the dry way. The natural material was reported to break down at about 925° with the formation of spinel. According to Roy, this single crystalline phase persisted above the solidus and apparently is on the liquidus above 1550°. In a detailed study of the K_2O—MgO—Al_2O_3—SiO_2 system, Schairer (1954) prepared a glass of the anhydrous phlogopite composition ($n = 1{\cdot}566$) and investigated a portion of its thermal history. He found that the first crystals to appear on the liquidus at 1628° were forsterite. These were joined by leucite at 1478° and spinel at 1473°. The last liquid crystallized at 1428°. Since the plane in which the anhydrous phlogopite composition lies is not ternary, a more complete study is required to fix the nature of the final assemblage. This work is now being undertaken by Schairer. As is demonstrated below, the high-temperature assemblage formed in the presence of water consists of forsterite, leucite, and orthorhombic $KAlSiO_4$.[1] Synthetic phlogopite held at 1200° breaks down to the last-named assemblage of crystals plus vapour. The relation of these phases to phlogopite is shown in Fig. 1. Natural phlogopites held in the dry

[1] There are at least three forms of $KAlSiO_4$: kaliophilite, kalsilite, and orthorhombic $KAlSiO_4$. Kalsilite is stable up to about 840°C, where it transforms into the orthorhombic form which persists to the liquidus (Tuttle and Smith, personal communication, 1953). Kaliophilite has been synthesized in the presence of fluxes (Kunze, 1954); however, its stability relations have not been determined. It changes into the orthorhombic form at about 1540°C (Bowen, 1917, p. 125).

way at temperatures above 1000° usually formed forsterite first, then leucite, and finally either orthorhombic $KAlSiO_4$, or spinel, or both, depending on its composition. In no case did spinel form first. A study of the quaternary system indicates that spinel would crystallize first from more alumina-rich compositions. For this reason, it is believed that the natural phlogopite used by Roy was not close to the ideal composition.

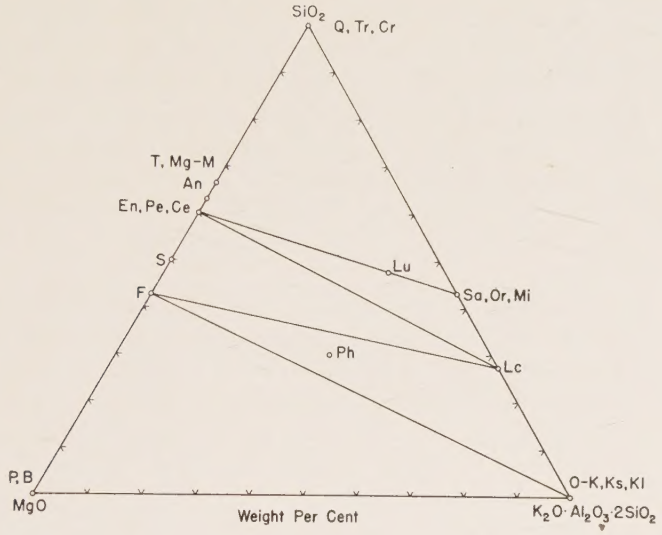

Fig. 1. A one-point projection of the system $MgO—SiO_2—K_2O \cdot Al_2O_3 \cdot 2SiO_2—H_2O$ showing the position of phlogopite, a trioctahedral mica, and of leucophyllite, a dioctahedral mica. The abbreviations are defined in Table 1.

Natural phlogopite

Three ordered polymorphs of phlogopite are known from single-crystal studies: one-layer monoclinic (1M), two-layer monoclinic (2M), and three-layer trigonal (3T).[1] Of the 16 phlogopites studied by Hendricks and Jefferson (1939), 14 were found to be 1M, one 2M, and one 3T. Some 28 analyzed phlogopites were determined by Heinrich (1952, p. 3), of which only three were 2M, two 3T, and the rest 1M. The 1M and 3T polymorphs have been found in the same hand specimen of a pegmatite (Heinrich, 1953, p. 6) and a marble (Smith and Yoder, 1953). The 1M mica appears to occur throughout the entire thermal range of geological conditions, that is, from sediments to lavas. Therefore, from the studies so far undertaken of natural materials, no clues could be gained as to the relative stability ranges of the polymorphs. The possibility that the polymorphism of the natural micas may be dependent on factors other than pressure and temperature was still to be investigated.

[1] The three-layer trigonal phlogopite (3T) was described by Hendricks and Jefferson (1939, p. 746) as three-layer rhombohedral. According to the International Tables for X-ray Crystallography (1952, p. 10), the term trigonal is now preferred.

Method of Investigation

Equipment

The experiments were performed mainly with the use of the Tuttle apparatus as modified by Van den Heurk (1953). In addition, "cold-seal" bombs (Tuttle, 1949), sometimes referred to as "inverted test-tube" bombs, and Morey bombs (Morey and Ingerson, 1937) were used. In these kinds of apparatus a charge is held in a vessel in which the desired water pressure is maintained by a pump actuated by a regulator connected to a Bourdon pressure gauge. The pressure vessels are heated externally by means of cylindrical resistance furnaces controlled by suitable temperature regulators. The temperature is measured by means of a chromel-alumel or iron-constantan thermocouple inserted in a well in the pressure vessel close to the centre of the charge. The error in temperature measurement is less than $\pm 5°C$, and that of the pressure measurement is less than ± 400 psi (pounds per square inch).

The charges were placed in two sets of two platinum-foil crucibles, as described in a previous publication (Bowen and Tuttle, 1949, p. 441), so that an inner set of crucibles was always surrounded with material of identical composition. In this way the vapour reaching the charge contained in the inner crucibles was believed to be saturated with respect to the constituents present. This method of holding the charge was satisfactory for runs of short duration; however, on long runs (weeks or months), particularly at high temperatures, the composition of the charge changed. The extraction of silica by the circulating vapour was the chief difficulty, although there is little doubt that other constituents were removed too. In order to overcome the changes of composition during these long runs, the charge was sealed with an excess of water in an annealed platinum tube 2 cm long, 2·5 mm inside diameter, having a 0·2 mm wall. The tubes were held in the apparatus in the same manner as the crucibles. The pressure was transmitted, however, by the collapse of the easily malleable wall of the tube. In this way circulation was prevented and no changes of composition were observed during the longest runs (six months). The principal disadvantage in experiments run in this fashion is that the pressure must be applied first and the charge undergoes a period of rising temperature, reaching the desired temperature in approximately half an hour. The crystallization which usually takes place during the run up period may be determined by quenching. When open crucibles are used, the temperature is applied first and no water is permitted to reach the charge until the desired temperature is obtained. In general it was found that at the same pressure and temperature crystal growth was faster in open crucibles than in sealed tubes.

The various pressure vessels, or bombs, described above are limited in temperature and pressure range (see Van den Heurk, 1953, p. 996), and it was necessary to use a more complicated system for runs at extreme conditions. The construction of the apparatus (Yoder, 1950, pp. 827–829) and its use in systems involving a volatile component are described elsewhere (Yoder, 1952a, p. 1318). In brief, the charge is contained in a sealed platinum tube which is held in an internally heated pressure vessel. The pressure is applied on the tubes through the medium of argon

gas. The temperature is measured by a platinum-platinum 10 rhodium thermocouple and the pressure is measured by the change in resistance of a calibrated manganin coil.

Initial materials

Previous experience indicated that if the stable assemblage was to be ascertained it was necessary to demonstrate a reaction with all possible initial materials for which the requisite compositions could be obtained. For this reason combinations of dry oxides, synthetic and natural minerals, glasses, or combinations of these materials were tried under the various conditions of temperature and pressure. For a given composition the conditions of a run were often duplicated, differing only in the initial materials. After the nature of the equilibrium was established, one or more combinations of materials of the requisite composition were selected for detailed study on the basis of reaction rate and quality of product.

Most runs were made on a mixture of periclase, gamma alumina, and a glass, $K_2O{\cdot}6SiO_2$, prepared by SCHAIRER. Such a preparation is referred to as a "mix."

Well-formed crystals of synthetic phlogopite were prepared by heating the mix under hydrothermal conditions between 900° and 950° at 15,000 psi for periods of 5 to 24 hours. Runs on synthetic material were usually made in the following way. A charge of mix was placed in the bomb and the conditions described above were imposed. Then the conditions were changed to new values without removal of the charge from the bomb. Since it had been demonstrated that the former conditions always yielded excellent crystals of phlogopite, it was concluded that synthetic phlogopite constituted the entire charge at the outset of the newly imposed conditions.

A glass of the anhydrous phlogopite composition, having an index of refraction of 1·566, was carefully made by SCHAIRER. Quenching of the melt in mercury was essential to prevent the crystallization of forsterite.

Several natural phlogopites of known structure were kindly contributed by S. B. HENDRICKS (HENDRICKS and JEFFERSON, 1939, pp. 758, 760):

Locality	*U.S.N.M.*	*Polymorph*
Franklin, N.J.	C3644	1M
Burgess, Ontario	82459	1M
Burgess, Ontario	106758 (78218)[1]	2M
Masham, Quebec	R4463	3T

The natural 2M phlogopite (U.S.N.M. 106758) was used in the few attempts at seeding other preparations to induce the growth of the 2M polymorph. Another phlogopite from Burgess County, Ontario (U.S.N.M. C3679), having a 1M structure, was used for most of the runs in which the natural material was desired.

The one remaining preparation intended for use in the study of phlogopite, a triturated mica, requires mention. It had been found useful in the experiments on muscovite to grind a natural muscovite until no X-ray or electron diffraction

[1] Several books of mica from Burgess County, Ontario, had been assigned the number 78218 by the U.S. National Museum. The specimen having a 2M structure, used by HENDRICKS and JEFFERSON as well as the present writers, has been renumbered 106758.

pattern remained. This triturated material then served as an initial material for the hydrothermal treatment. Such an approach was not possible with phlogopite as a result of the failure to destroy the phlogopite structure by grinding. The natural phlogopite from Burgess County, Ontario (U.S.N.M. C3679) was ground dry in a power-driven agate mortar for 30 hours. Samples were taken every 4 hours and a powder X-ray diffraction pattern was made of the product. It was found that little change in the structure of the mica was produced. The relative behaviour of phlogopite and muscovite in grinding may account for the predominance of residual phlogopite (or biotite) over residual muscovite in some fine-grained sediments.

Distilled water was present in excess in all experiments. When sealed tubes were employed equal weights of solid material and water were used.

Method of identification

One of the principal difficulties in hydrothermal experimentation is the identification of the fine-grained products. Resort was made to X-ray diffraction patterns and to optical properties when the products were coarse grained, or when the initial stages of a reaction were being investigated. Help was gained as well from the electron microscope and electron diffraction studies of M. Swerdlow of the U.S. National Bureau of Standards.

The Norelco Geiger-counter X-ray spectrometer, capable of recording the back-reflection region, was employed for the fine-grained materials. The layered minerals present a special problem in the preparation of a suitable mount for this and other powder X-ray diffraction techniques. For routine identification a thin, even layer of the finely powdered sample is spread on a glass microscope slide, with acetone[1] as a medium. As a result of the use of this method the natural micas exhibit considerable preferred orientation even though they are ground to less than 5 microns in particle size. The fine-grained nature of the synthetic products, on the other hand, is a distinct advantage; since each grain contains many orientations, excellent patterns devoid of preferred orientation are obtained.

For those natural micas of which there was sufficient material, a suitable, but not entirely satisfactory, mount was prepared by dusting the powdered sample in a shallow aluminium cell having a glass slide as a bottom. After the cell is filled, another glass slide is placed on the top and the cell is inverted. The bottom slide, now on top, is removed without sliding, and a smooth layer of sample is achieved, having a greatly reduced preferred orientation.[2] If the natural mica occurs in sheets or large flakes, these are cut into squares and stacked in books. Held in a hand vise, the books are filed on edge, producing a coarse powder. The powder so produced by filing, or as obtained directly, is then ground in acetone in a power-driven agate mortar for at least four hours. The minus 325 sieve product is used in the normal acetone mount.

Weissenberg, Laue and precession techniques were used when suitable single

[1] This organic reagent did not produce any change in the basal spacing of the micas. That is, no expansion or swelling in the structure of the micas, such as is observed for some layered minerals with glycerol (MacEwan, 1946) or ethylene glycol (Bradley, 1945), resulted from immersion in acetone.

[2] Similar methods have been successfully employed by G. L. McCreery (Beatty, 1949) and Hildebrand (1953).

crystals were available. The account of this work was reported by SMITH and YODER (1953, p. 1475); however, the results are briefly mentioned where necessary in the present paper.

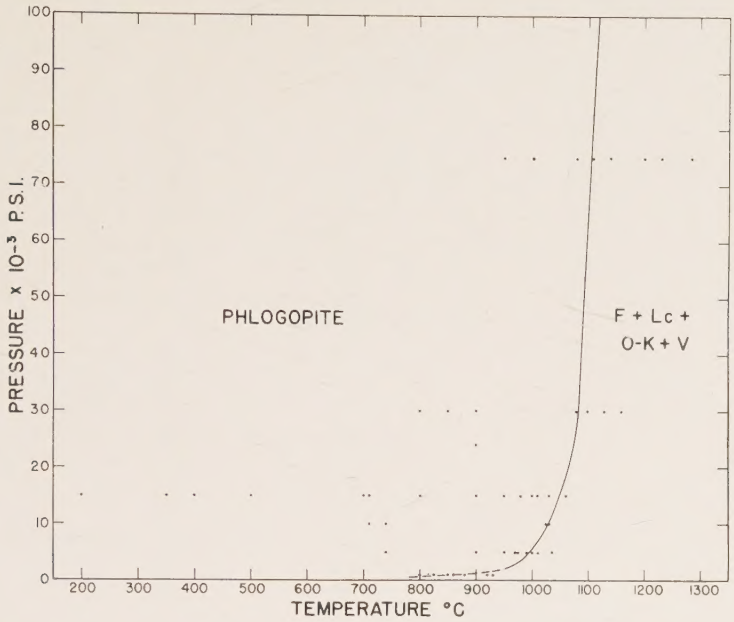

Fig. 2. The upper stability curve of synthetic phlogopite deduced from data given in Table 2. Each dot represents the pressure and temperature conditions of one or more runs.

EXPERIMENTAL RESULTS

Data

The results of the experiments on materials of the phlogopite composition are given in Table 2. The abbreviations used to designate the phases are given in Table 1. Those runs marked with an asterisk were performed in a sealed platinum tube. The stability range of synthetic phlogopite deduced from these data is shown in Fig. 2.

Table 1. *Abbreviations used to designate phases*

B	Brucite	Mg—M	Magnesian montmorillonite
Ce	Clinoenstatite	O—K	Orthorhombic $KAlSiO_4$
Cr	Cristobalite	P	Periclase
En	Enstatite	Pe	Protoenstatite
F	Forsterite	Ph	Phlogopite
Ka	Kaolinite	Q	Quartz
Kl	Kaliophilite	S	Serpentine
Ks	Kalsilite	Sa	Sanidine
Lc	Leucite	Tr	Tridymite
Lu	Leucophyllite	V	Vapour

Table 2. Results of hydrothermal treatment of various materials of the phlogopite composition

Temp. °C	Pressure × 10^{-3} psi	Time hours	Products
		(*a*) *Mix*	
930	1	110	F + Lc + O—K
880	1	46	F + Lc + O—K
860	1	334	F + Lc + O—K
850	1	164	F + Lc + O—K
825	1	164	F + Lc + O—K
800	1	48	F + Lc + O—K
800	1	336	F + Lc + O—K + Ph
1035	5	1	F + Lc + O—K
1010	5	1	F + Lc + O—K
990	5	10	Ph + F + Lc + O—K
975	5	21	Ph + F + Lc + O—K
970	5	1	F + Lc + O—K
950	5	14	Ph + F + Lc + O—K
900	5	330	Ph
900	5	1	Ph + F + Lc + O—K
750	5	340	Ph
750	5	164	Ph
1025	10	11	Ph + F + Lc + O—K
750	10	165	Ph
710	10	403	Ph
1060	15	0·5	F + Lc + O—K
1030	15	0·8	Ph + F + Lc + O—K
1010	15	1	F + Lc + O—K
1000	15	14	Ph
1000	15	1	Ph + F + Lc + O—K
980	15	22	Ph
950	15	5	Ph
900	15	769	Ph
900	15	183	Ph
900	15	66	Ph
*900	15	52	Ph + F
900	15	24	Ph
800	15	163	Ph
800	15	24	Ph
710	15	208	Ph + F + O—K
700	15	18	Ph
500	15	87	Ph
400	15	1296	Ph (1Md?) + Ka
400	15	376	Ph (1Md?)
*350	15	2208	Ph (1Md?)
*200	15	4120	Ph (1Md?)

Table 2 (continued)

(*a*) *Mix (continued)*

Temp. °C	Pressure × 10^{-3} psi	Time hours	Products
900	24	172	Ph
900	30	70	Ph
850	30	49	Ph
*800	30	1826	Ph
*800	30	502	Ph
*800	30	130	Ph
*800	30	46	Ph

(*b*) *Synthetic phlogopite*

920	1	38	F + Lc + O—K
880	1	39	Ph + F + Lc + O K
850	1	140	Ph + F + Lc + O K
825	1	308	Ph
1000	5	21	Ph + F + Lc + O K
1030	10	9	Ph + F + Lc + O K
1060	15	0·2	Ph + F + Lc + O K
*1160	30	5	F + Lc + O—K
*1130	30	5	Ph + F
*1100	30	6	Ph + F + Lc
*1080	30	5	Ph
*1285	75	5	Ph + F
*1230	75	6	Ph + F
*1200	75	5	Ph + F
*1140	75	5	Ph + F
*1110	75	5	Ph + F + Lc
*1080	75	5	Ph + F
*1000	75	5	Ph

(*c*) *Natural phlogopites*

(i) Burgess Co., Ontario. U.S.N.M. C3679, 1M

1060	15	0·2	1M or 3T Ph
1020	15	4	1M or 3T Ph
950	15	138	1M or 3T Ph
950	15	48	1M or 3T Ph
500	15	167	1M or 3T Ph
400	15	1296	1M or 3T Ph
*1160	30	5	1M or 3T Ph
*1130	30	5	1M or 3T Ph
*1100	30	6	1M or 3T Ph
*1080	30	5	1M or 3T Ph

Table 2 (continued)

(c) Natural phlogopites (continued)

Temp. °C	Pressure × 10^{-3} psi	Time hours	Products
*1285	75	5	1M or 3T Ph + F
*1230	75	6	1M or 3T Ph + F
*1200	75	5	1M or 3T Ph + F
*1140	75	5	1M or 3T Ph + F
*1080	75	5	1M or 3T Ph
	(ii) Burgess Co., Ontario. U.S.N.M. 106758. 2M		
*900	15	769	2M Ph + 1M or 3T Ph
*1140	75	5	1M or 3T Ph + F
*1110	75	5	1M or 3T Ph + F
*1000	75	5	1M or 3T Ph
	(iii) Burgess Co., Ontario. U.S.N.M. 82459. 1M		
900	15	769	1M or 3T Ph
900	15	88	1M or 3T Ph
900	15	1	1M or 3T Ph
400	15	1296	1M or 3T Ph
	(iv) Masham, P.Q. U.S.N.M. R4463. 3T		
900	15	769	1M or 3T Ph
900	15	1	1M or 3T Ph
400	15	1296	1M or 3T Ph
	(d) Glass		
800	15	2	Ph + F
*1130	30	0·5	Ph + F
*800	30	1826	Ph + F + Lc + O—K
*800	30	1	Ph
	(e) Mix seeded with 2M phlogopite (U.S.N.M. 106758)		
*680	30	980	1M or 3T Ph
*600	30	1532	1M or 3T Ph
*500	30	1940	1M or 3T Ph
*400	30	1940	1M or 3T Ph
*200	30		

* Sample contained in sealed platinum tube.

Phlogopite grows very quickly as thin, colourless plates, approximately hexagonal in outline, up to 0·5 mm in diameter (Fig. 3). Their optical properties are as follows:

	Yoder *and* Eugster	Kunitz, 1924	Winchell, 1951
	synthetic	*estimate*	*estimate*
α	1·548	1·544	1·535
γ	1·588	1·578	1·565
2V	small or 0°	—	10° ca.

The optical properties for pure phlogopite were estimated by Kunitz and by Winchell from those of analyzed natural phlogopites. The measurements of indices of refraction of the synthetic crystals were made in sodium light and are believed to be accurate to $\pm$0·003. The average index of refraction calculated from the Gladstone and Dale relation using the specific refractive energies given by Larsen and Berman (1934, p. 31) is 1·582. The crystals characteristically exhibit high birefringence in transverse sections and low birefringence on the plates.

The measured density is 2·79 $\pm$ 0·03 and the density calculated from the unit cell data (see following section) is 2·780 $\pm$ 0.010. The water content of synthetic phlogopite was determined on two 10 mg samples carefully prepared in sealed platinum tubes at 900°C, 15,000 psi, for a period of 5 days. The H_2O^+ contents were 4·36% and 4·40% and the error of measurement is $\pm$0·12%. The potash content of two 20 mg samples of synthetic phlogopite prepared under identical conditions was determined by the flame photometer method. The K_2O contents were 11·2% and 11·8% and the error is believed to be $\pm$0·5%. The water and potash contents of an ideal phlogopite are 4·31% and 11·29%, respectively.

The reaction indicated by the univariant curve in Fig. 2 is the following:

2 phlogopite $\rightleftharpoons$ 3 forsterite + leucite + orthorhombic $KAlSiO_4$ + 2 water

The solid phases on the right-hand side of the reaction often grow metastably in the region where phlogopite is stable, particularly under those conditions immediately to the left of the pressure-temperature curve. In such regions the growth of phlogopite by reaction of the metastable phases is very slow. For this reason great care had to be exercised in evaluating the data. The stability curve of phlogopite is based on observations involving the growth and breakdown of the synthetic crystals. At the lowest pressures investigated (1000 psi), however, the reaction rate proved to be so slow that further experiments at even lower pressures were considered not practical. A method for obtaining the upper stability limits of phlogopite to atmospheric pressure will be presented in a later section.

The pure anhydrous phlogopite composition would be expected to consist of approximately 53% forsterite, 27% leucite, and 20% $KAlSiO_4$ by weight. Natural phlogopite is known to occur with forsterite, leucite, and kalsilite, the low-temperature form of $KAlSiO_4$ (Federico and Fornaseri, 1952; Holmes, 1942).

The breakdown of natural phlogopite above its stability range under hydrothermal conditions appears to be a very slow process. Only forsterite was observed at the edges of the natural crystals at the end of the longest runs. This breakdown behaviour is illustrated in Fig. 4. In addition to the crystals of forsterite easily

recognized by their high relief in the photomicrograph, needles are also seen subparallel to the prism planes. By gently heating in hydrofluoric acid it was possible to dissolve away most of the phlogopite and forsterite until only the needles remained. These were identified as mullite and are believed to be a metastable product of decomposition. They were not present in sufficient amount to be detected in the powder X-ray diffraction pattern of the decomposing mica. The analogous metastable formation of mullite during the decomposition of muscovite has been observed by Sundius and Byström (1953, p. 635).

As can be seen from the data in Table 2c, some of the natural phlogopites persisted in part well above their stability limit. The reason for this behaviour where sealed tubes were employed may lie in the following circumstances. The initial material consisted of natural mica ground for 4 hours in acetone in a power-driven agate mortar. The grain size was estimated to be 5 microns or less. During the half-hour period required to obtain the desired temperature at the chosen pressure, the ground mica recrystallizes into well-formed plates, hexagonal in outline, up to 0·1 mm in diameter (Fig. 5). It is these well-formed crystals which apparently are very slow in decomposing. The recrystallized material gives a powder X-ray diffraction pattern having sharper and more intense peaks than the ground mica.

Polymorphism

A large number of experiments were aimed primarily at the determination of the stability ranges of the various polymorphs of phlogopite. Attempts were made to make single-crystal studies of the largest synthetic crystals, but those crystals were found to be too thin to give adequate intensities even with long exposures. Although the natural polymorphs are readily distinguished by single-crystal studies, their identification by means of powder X-ray diffraction patterns presents difficulties. The powder X-ray diffraction patterns of natural 1M, 2M, and 3T polymorphs of phlogopite previously determined by single-crystal techniques are given with synthetic phlogopite in Fig. 6. It is readily seen that the patterns of 1M, 3T, and synthetic mica are identical except for minor variations of intensity due to preferred orientation, and differ from 2M. A study of the lattice parameters and intensities of the Weissenberg patterns of the natural 1M and 3T polymorphs by J. V. Smith (Smith and Yoder, 1953) led to the conclusion that their powder X-ray diffraction patterns would be indistinguishable within the limits of measurement. The reflections of the powder X-ray diffraction pattern can be indexed equally well on a 1M or a 3T cell (Table 3). The parameters of the unit cells were found to be:

1M (*Cm*)	*3T*($P3_112$ *or* $P3_212$)
$a = 5{\cdot}314 \pm 0{\cdot}01$ Å	$a = 5{\cdot}314 \pm 0{\cdot}01$ Å
$b = 9{\cdot}204 \pm 0{\cdot}02$ Å	$c = 30{\cdot}480 \pm 0{\cdot}01$ Å
$c = 10.314 \pm 0{\cdot}005$ Å	
$\beta = 99° 54' \pm 5'$	

These values are in accord with those determined from single-crystal data for natural phlogopites by Hendricks and Jefferson (1939, p. 770) and by Smith and Yoder (1953).

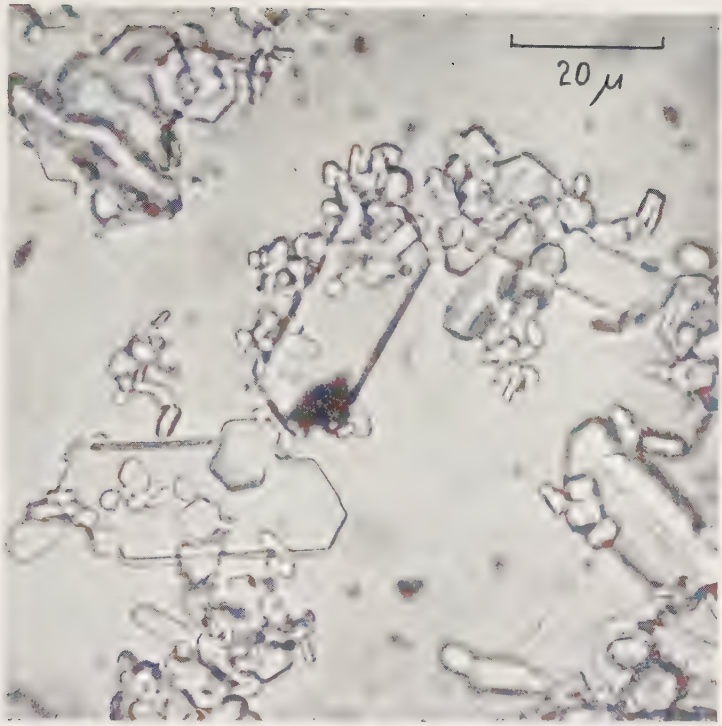

Fig. 3. Photomicrograph of synthetic phlogopite prepared at 1080°C, 75,000 psi water vapour pressure, and held for 5 hours in a sealed platinum tube.

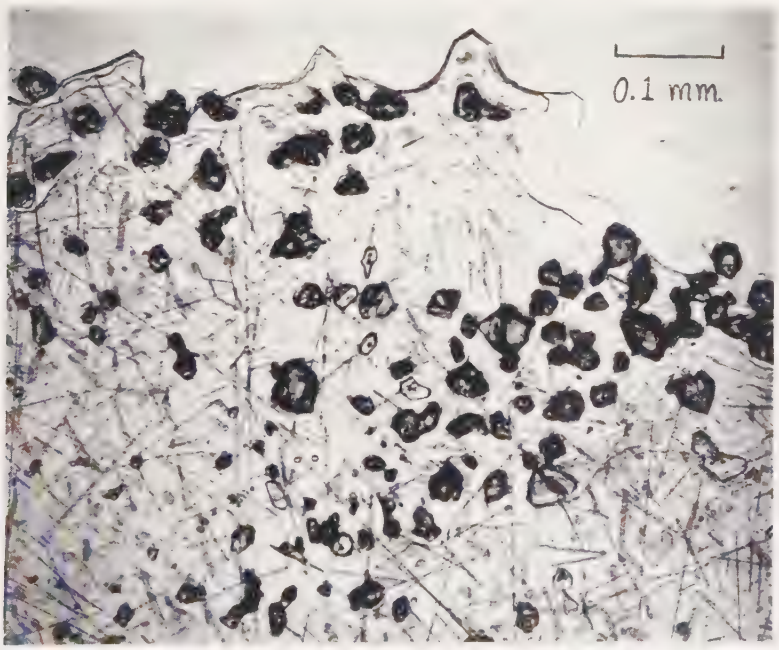

Fig. 4. Photomicrograph showing initial decomposition products of a natural phlogopite. Crystals of high relief are forsterite and the needles are mullite. Some apparent needles are the edges of recrystallized phlogopite (see Fig. 7).

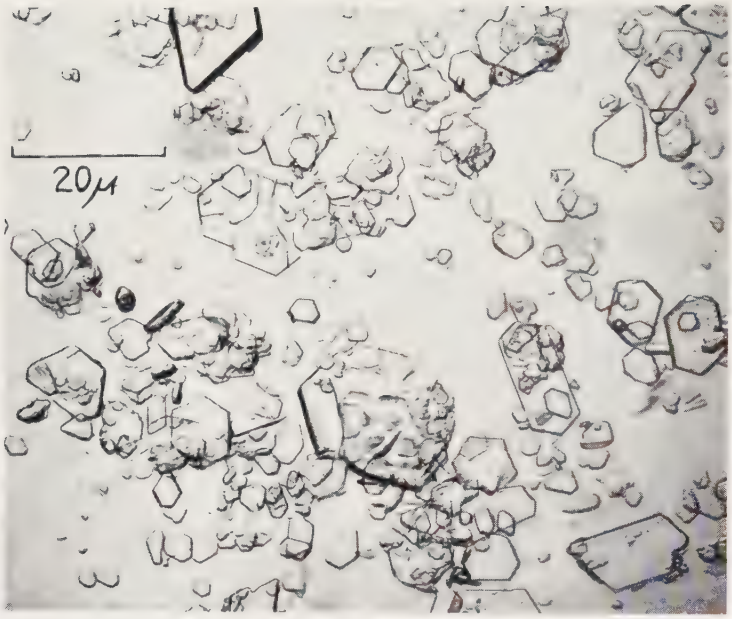

Fig. 5. Photomicrograph of recrystallized natural phlogopite ground for 4 hours in acetone and held at 1200°C, 75,000 psi water vapour pressure for 5 hours in a sealed platinum tube. The crystals grew during the run-up period. No decomposition is observed.

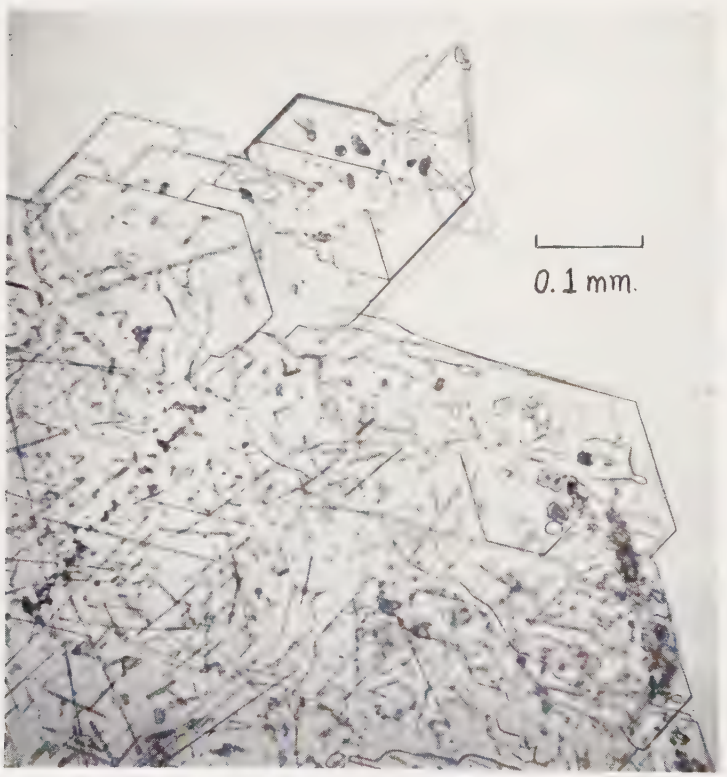

Fig. 7. Photomicrograph of recrystallized single crystal of a natural phlogopite (U.S.N.M. 106758) held at 1000°C, 75,000 psi water vapour pressure for 5 hours. Note the traces of new plates formed parallel to and at an angle to the basal section of the original single crystal.

Attempts were also made to determine the polymorphic form of the synthetic crystals by optical means. Most natural 1M phlogopites are reported to have a 2V of about 5° to 7°, and the 3T phlogopites would be expected to have a 2V equal to 0° even though many uniaxial minerals are anomalously biaxial. Again the synthetic crystals proved to be too thin to measure 2V with the necessary accuracy. Resort was also made to the conversion of a single crystal of a known natural 2M mica to

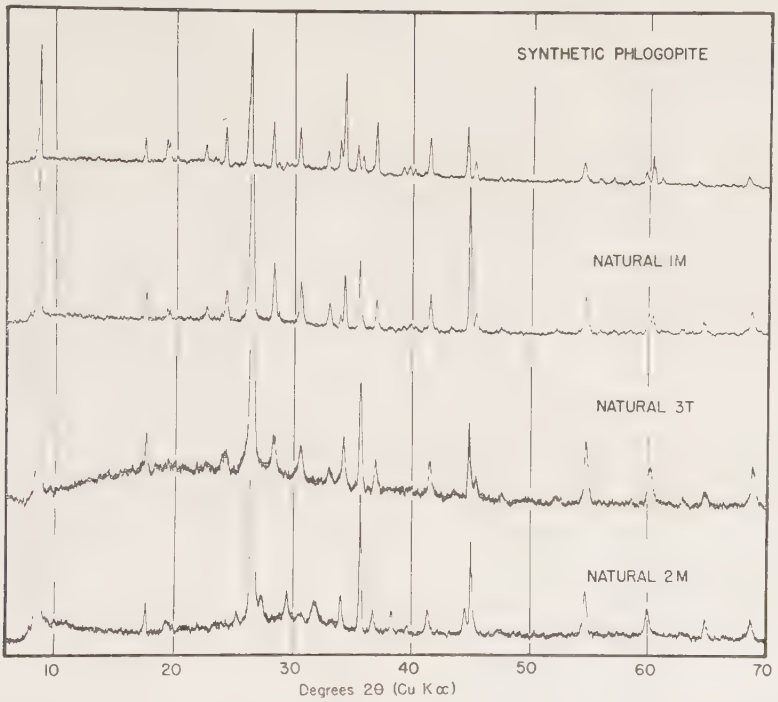

Fig. 6. Photograph of powder X-ray diffraction patterns of a synthetic phlogopite produced at 950°C, 15,000 psi water vapour pressure for 5 hours, a natural 1M phlogopite (U.S.N.M. C3679), a natural 3T phlogopite (U.S.N.M. R4463), and a natural 2M phlogopite (U.S.N.M. C3675).

1M or 3T by hydrothermal treatment. The 2M crystal did partially invert to a 1M or a 3T polymorph, but the single crystal became a multitude of well-formed plates hexagonal in outline, prohibiting its use as a single crystal (Fig. 7). Of particular interest is the observation that some of the newly formed plates are subperpendicular to 001 and subparallel to the {100} prism of the original single crystal. Although the reason for this behaviour is not understood, it does suggest that some cross-mica schists may have arisen through a recrystallization mechanism other than one controlled by stress.

Only one experiment yielded a clue to the relative stability of the polymorphs. A natural 2M was partially transformed into a 1M or a 3T at 900° and 15,000 psi after more than a month. The equivalent transformation was obtained for a natural 2M biotite, the details of which will be reported in a later paper. It is concluded that at 900° a 1M or a 3T phlogopite is more stable than a 2M. Experiments

at lower temperatures and of longer duration resulted in no observable changes in the natural mica polymorphs.

Table 3. *Powder X-ray diffraction data for a synthetic phlogopite*

$2\theta_{obs}$	$Q_{obs} \times 10^5$	1M *hkl*	$\Delta Q \times 10^5$	3T *hkl*	*I*	*d*
8.705	0972	001	−3	0003	>100	10·157
17·465	3878	002	−3	0006	25	5·078
19·310	4733	020	−12	$10\bar{1}0$	10	4·596
19·515	4833	110	−4	$10\bar{1}1$	10	4·549
22·570	6444	111	−1	$10\bar{1}4$	15	4·120
22·240	7418	$11\bar{2}$	−6	$10\bar{1}5$	30	3·672
26·140	8605	022	−9	$10\bar{1}6$	40	3·409
26·310	8716	003	2	0009	>100	3·387
28·210	9994	112	1	$10\bar{1}7$	40	3·163
30·455	11608	$11\bar{3}$	2	$10\bar{1}8$	30	2·944
32·835	13442	023	−2	$10\bar{1}9$	15	2·728
33·870	14278	130 $20\bar{1}$	−7	$11\bar{2}1$	15	2·646
34·240	14582	200 $13\bar{1}$	12	$11\bar{2}2$	55	2·619
35·295	15491	004 113	9 −6	00012 $10\bar{1}10$	25	2·541
35·745	15875	131 $20\bar{2}$	10	$11\bar{2}4$	7	2·510
36·880	16864	$13\bar{2}$ 201	−10	$11\bar{2}5$	30	2·435
39·220	18985	$22\bar{1}$	7	$20\bar{2}1$	5	2·295
39·630*b*	19368	220 132 $20\bar{3}$	−53 69	$20\bar{2}2$ $11\bar{2}7$	5	2·272
40.140	19850	041	3	$20\bar{2}3$	3	2·244
40·905	20580	$22\bar{2}$	−26	$20\bar{2}4$	3	2·204

Table 3 (*continued*)

$2\theta_{obs}$	$Q_{obs} \times 10^5$	1M *hkl*	$\Delta Q \times 10^5$	3T *hkl*	*I*	*d*
41·410	21070	$13\bar{3}$ 202	−18	$11\bar{2}8$	20	2·179
41·920*b*	21568	221	+9	$20\bar{2}5$	2	2·153
44·560	24228	005	−9	00015	50	2·032
45·250	24945	$20\bar{4}$ 133	−18	$11\bar{2}10$	10	2·002
47·390	27221	$13\bar{4}$ 203	−34	$11\bar{2}11$	3	1·917
52·000	32391	$20\bar{5}$ 134	−37	$11\bar{2}13$	3	1·757
52·650	33147	150 $24\bar{1}$	8	$21\bar{3}1$	3	1·742
54·440	35265	$13\bar{5}$ 204	−5	$11\bar{2}14$	15	1·684
55·840	36955	$31\bar{3}$ 311	−33	$21\bar{3}6$	5	1·645
56·960	38327	$24\bar{3}$ 152	−6	$21\bar{3}7$	5	1·615
58·260	39942	$15\bar{3}$ 242	−6	$21\bar{3}8$	5	1·582
59·700	41757	$20\bar{6}$ $31\bar{4}$	9	$21\bar{3}9$	10	1·547
60·275	42489	060	0	$30\bar{3}0$	25	1·534
61·020	43444	061 330	14	$30\bar{3}3$	3	1·517

$2\theta_{obs}$ in degrees; CuKα 0°–35° $\lambda = 1{\cdot}5418$
CuKα_1 35°–70° $\lambda = 1{\cdot}5405$

d = interplanar spacing in Å
$Q = 1/d^2$
$\Delta Q = Q_{calc} - Q_{obs}$
b = broad peak
I = relative intensity based on arbitrary linear scale

On the basis of the fact that only 1M phlogopites have been found in lavas, it is the opinion of the writers that the synthetic product is more likely 1M than 3T. It can be said with certainty that the synthetic crystals are not 2M. For

Table 4. Powder X-ray diffraction data for a natural 2M phlogopite (U.S.N.M. 106758)

$2\theta_{obs}$	$Q_{obs} \times 10^5$	$\Delta Q \times 10^5$	*hkl*	*I*	*d*
8·730	975	8	002	>100	10·129
17·540	3912	19	004	18	5·056
19·240	4699	0 −1	110 020	19	4·612
19·660*b*	4905	39	021	7	4·515
21·785*b*	6009	−1	112	5	4·079
23·325	6876	33	023	18	3·814
25·155	7979	0	$11\bar{4}$	33	3·540
26·495	8837	8	006	>100	3·362
27·165	9281	0	114	38	3·283
28·280	10042	−15	$11\bar{5}$	9	3·156
29·380	10821	19	025	40	3·040
30·555	11683	−28	115	8	2·926
31·750	12591	−24	$11\bar{6}$	22	2·818
33·815*b*	14233	−54	$13\bar{1}$	22	2·651
34·165	14520	1	116	>100	2·624
35·595	15721	4	008	28	2·522
36·840	16801	−6	133	40	2·439
38·115*b*	17941	−63	117	16	2·361
39·080*b*	18824	−26 −32	220 040	9	2·304
39·705*b*	19407	17	$13\bar{5}$	9	2·270
41·470	21034	18	135	45	2·180
44·435	24060	−29	224	21	2·039

Table 4 (continued)

$2\theta_{obs}$	$Q_{obs} \times 10^5$	$\Delta Q \times 10^5$	*hkl*	*I*	*d*
44·940	24578	−8	0010	66	2·017
45·340*b*	24995	0	$13\bar{7}$	20	2·000
47·515*b*	27311	−36	137	5	1·914
52·255*b*	32612	−81	139	3	1·751
52·700*b*	33151	−32	227	5	1·737
54·735	35562	24	153	47	1·677
60·165	42281	1 15	060 330	50	1·538
60·890*b*	43209	54	062	10	1·521

$2\theta_{obs}$ in degrees; CuKα $\lambda = 1{\cdot}5418$ Å
b = broad peak
d = interplanar spacing in Å
$Q = 1/d^2$
$\Delta Q = Q_{calc} - Q_{obs}$
I = relative intensity based on arbitrary linear scale. Not reliable because of preferred orientation.

comparison the powder X-ray diffraction data for a natural 2M phlogopite are given in Table 4. The cell parameters for that phlogopite, on the basis of a 2M cell having the space group C2/c, are:

$$a = 5{\cdot}347 \pm 0{\cdot}01 \text{ Å}$$
$$b = 9{\cdot}227 \pm 0{\cdot}01 \text{ Å}$$
$$c = 20{\cdot}252 \pm 0{\cdot}005 \text{ Å}$$
$$\beta = 95^\circ\ 1' \pm 5'$$

These values are in accord with those found by other workers.

A few remarks should be made about the character of the mica produced at the lowest temperatures, i.e., below 400°C. An example of the powder X-ray diffraction pattern for these micas is given in Fig. 8A. It was found that only the 0*k*0, *h*00, 00*l*, and 20*l* reflections are present for 2θ less than 70° and all the *hkl* reflections are absent. It is believed that these crystals consist of randomly stacked units of 1M and are designated by the symbol 1Md (see Hendricks, 1939, p. 536; Strese and Hofmann, 1941; Smith and Yoder, 1953). In muscovite an analogous structural relation exists: a 1Md is slowly ordered to 1M with hydrothermal treatment (Yoder and Eugster, 1953, p. 1496). This ordering process in phlogopite is demonstrated in Figs. 8A to 8D. The possible occurrence of 1Md in sediments and its relation to the trioctahedral clay micas are discussed in a later section.

The micas produced below 400° were tested with glycerol and ethylene glycol and showed no structural expansion characteristics. These results remove the possibility that the layered mineral produced might be a montmorillonite.

Thermodynamic considerations

It was pointed out above that the stability curve of phlogopite at the lowest pressures was not fixed with certainty because of the slow rate of reaction. However, the stability curve may be obtained for the lowest pressures by calculation

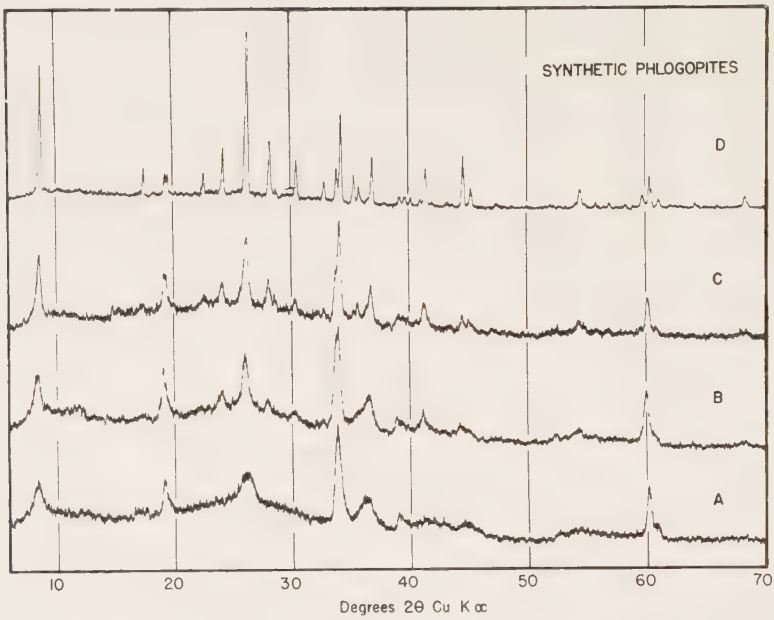

Fig. 8. Photograph of powder X-ray diffraction patterns showing growth characteristic of synthetic phlogopite from low temperatures (A) to high temperatures (D).

using the data obtained at higher pressures. The integrated form of the Clausius-Clapeyron equation permits the calculation of equilibrium temperatures for specific pressures, provided the enthalpy of the reaction is known. Three assumptions are involved in the equation:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H}{R}\left(\frac{(T_2 - T_1)}{T_1 T_2}\right)$$

where P is the pressure; T, the temperature; ΔH, the enthalpy of reaction; and R, the gas constant. The first assumption is that the specific volume of the vapour is negligible. This can be justified when the pressure is low and the molar volume of the vapour is large. The second assumption is that the volume of the vapour, V, can be expressed by the ideal gas law, $PV = RT$. Thirdly, the enthalpy is assumed not to be a function of temperature. These assumptions can best be justified by the fact that the integrated equation does fit the experimental data in a large number of cases.

For the phlogopite reaction, the following equilibrium values were obtained from Fig. 2 after appropriate conversion:

Pressure (atm.)	*Temperature (°K)*
(68)	(1123)
340	1268
680	1298
1020	1323
2040	1358
5100	1398

(One doubtful point on the equilibrium curve is indicated by brackets.) The enthalpy is obtained from a plot of log P vs. $1/T$ where the slope is $-\Delta H/2{\cdot}303R$. The ΔH for the reaction is essentially constant in the region of lower pressure as

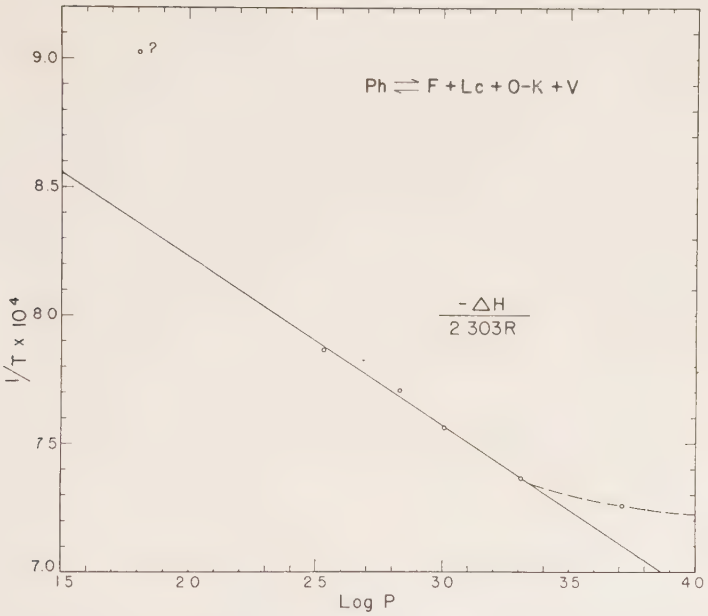

Fig. 9. Plot of univariant curve of equilibrium data for the reaction Ph ⇌ F + Lc + O—K + V for the purpose of obtaining the enthalpy of reaction, ΔH. The logarithmic scale emphasizes the error at the lowest pressure.

indicated in Fig. 9, and the assumptions are justified provided the value at 1000 psi is accepted as inaccurate for reasons already given.[1] Using the value of ΔH obtained in this way, 69·1 kcal/mol, the equilibrium temperature is calculated for one atmosphere and 68 atmospheres (= 1000 psi) water vapour pressure to be 770° and 925°C, respectively. These temperatures are of great importance in

[1] The measured temperature at 1000 psi water vapour pressure appears to be greatly in error; however, the position of the determined curve is only slightly displaced from the calculated curve in the low pressure region.

The point representing the equilibrium determined at the highest pressure does not satisfy the stated assumptions. Such departures from the conditions imposed by the assumptions are to be expected at the higher pressures and temperatures.

considerations of the stability limit of phlogopite under low partial vapour pressures of water and high total pressures (see for example MacDonald, 1953).

Role of fluorine

Based on some 50 specimens of phlogopite and biotite for which fluorine was analyzed, the average mica of those compositions contains 1·4% fluorine. The synthesis of the fluorophlogopite has been accomplished by many investigators, and its congruent melting point under one atmosphere of fluorine was fixed at about 1345°C by Van Valkenburg and Pike (1952). The substitution of F for OH appears to result in a rise of 575°C in the upper stability limit at one atmosphere pressure! The stability limits of the hydroxyl- and fluorine-bearing micas are not comparable, since in one case water vapour is a product and in the other, presumably SiF_4 or more complex fluorides. The partition of F and OH between vapour and crystals is not known. For these reasons the influence of fluorine on the stability range of the natural micas cannot be evaluated. However, it should be mentioned that two natural phlogopites containing fluorine decomposed at temperatures close to those of pure phlogopite (see Table 2c).

Although the upper stability curve was not established, runs on fluorophlogopite compositions were made by the present writers in the hope that some knowledge of the polymorphism might be gained. Since fluorophlogopite grows quickly it was thought that the stability range of the various polymorphs could be readily obtained. Under a series of temperatures up to 1010°C at 5000 psi pressure only a 1M or a 3T fluorophlogopite was obtained. The powder X-ray diffraction data for the synthetic fluorophlogopite are given in Table 5. The unit cell parameters are:

1M (*Cm*)	*3T*($P3_112$ *or* $P3_212$)
$a = 5{\cdot}310 \pm 0{\cdot}01$ Å	$a = 5{\cdot}494 \pm 0{\cdot}01$ Å
$b = 9{\cdot}195 \pm 0{\cdot}02$ Å	$c = 29{\cdot}943 \pm 0{\cdot}01$ Å
$c = 10{\cdot}136 \pm 0{\cdot}005$ Å	
$\beta = 100° 4' \pm 3'$	

Samples of fluorophlogopite made by the U.S. National Bureau of Standards and by the U.S. Bureau of Mines Electrotechnical Laboratory were found to have the same powder X-ray diffraction pattern.[1] It was not possible, therefore, to fix the stability range of the natural mica polymorphs by investigating the fluorine-bearing analogue.

A comparison of the unit cell data for hydroxyl-bearing and fluorine-bearing phlogopites indicates that the *c* parameters are sufficiently different to distinguish them on the basis of powder X-ray diffraction patterns. It should be pointed out that the substitution of other atoms in phlogopite may also cause a contraction of

[1] The density and indices of refraction of fluorophlogopite are given:

	Mines	*Standards*
α	1·522	1·519
γ	1·549	1·547
ρ	2·847	3·00

The average index of refraction calculated from the Gladstone and Dale relation is 1·564 and the density computed from the above unit cell data is 2·979.

Table 5. Powder X-ray diffraction data for a synthetic fluorophlogopite

$2\theta_{obs}$	$Q_{obs} \times 10^5$	1M *hkl*	$\Delta Q \times 10^5$	3T *hkl*	*I*	*d*
8·855	1002	001	2	0003	80	10·042
17·730	3996	002	20	0006	5	5·002
19·335	4745	020	−14	$10\bar{1}0$	12	4·590
19·535	4843	110	−1	$10\bar{1}1$	11	4·544
20·190	5168	$11\bar{1}$	9	$10\bar{1}2$	5	4·398
22·720	6527	111	−11	$10\bar{1}4$	14	3·914
24·410	7520	$11\bar{2}$	0	$10\bar{1}5$	21	3·646
26·355	8745	022	2	$10\bar{1}6$	36	3·382
26·775	9020	003	16	0009	>100	3·329
28·500	10196	112	1	$10\bar{1}7$	30	3·132
30·795	11863	$11\bar{3}$	7	$10\bar{1}8$	21	2·903
33·230	13758	023	9	$10\bar{1}9$	10	2·696
33·935	14331	130 $20\bar{1}$	−27	$11\bar{2}1$	17	2·649
34·375	14644	$13\bar{1}$ 200	−5	$11\bar{2}2$	37	2·609
35·895	15978	131 $20\bar{2}$	0	$11\bar{2}4$	9	2·502
37·035	16973	201 132	9	$11\bar{2}5$	24	2·427
39·255	18987	040	−37	$20\bar{2}0$	10	2·295
39·675	19379	220	−9	$20\bar{2}2$	8	2·272
39·970	19657	$20\bar{3}$ 132	2	$11\bar{2}7$	6	2·256
40·235	19939	041	−11	$20\bar{2}3$	8	2·241
41·045	20716	$22\bar{2}$	−7	$20\bar{2}4$	3	2·199

Table 5 (continued)

$2\theta_{obs}$	$Q_{obs} \times 10^5$	1M *hkl*	$\Delta Q \times 10^5$	3T *hkl*	*I*	*d*
41·690	21343	$13\bar{3}$ 202	−11	$11\bar{2}8$	18	2·166
42·070	21716	221	−3	$20\bar{2}5$	3	2·148
43·240	22882	042	58	$20\bar{2}6$	6	2·092
45·395	25096	005	3	00015	10	1·998
47·870	27743	203 $13\bar{4}$	−52	$11\bar{2}11$	3	1·900
52·585	33071	$20\bar{5}$ 134	−26	$11\bar{2}13$	3	1·739
55·105	36064	$13\bar{5}$ 204	−7	$11\bar{2}14$	14	1·665
55·985	37131	311	2	$21\bar{3}6$	3	1·641
56·540	37810	$22\bar{5}$	−34	$20\bar{2}13$	5	1·626
57·150	38561	152 $24\bar{3}$	21	$21\bar{3}7$	4	1·610
58·525	40273	$15\bar{3}$ 242	−17	$21\bar{3}8$	3	1·575
60·345	42578	060	1	$30\bar{3}0$	24	1·532
61·120	43573	330 061	10	$30\bar{3}3$	6	1·515

$2\theta_{obs}$ in degrees; 0°–50° CuKα $\lambda = 1{\cdot}5418$
50°–70° CuKα_1 $\lambda = 1{\cdot}5405$
d = interplanar spacing
$Q = 1/d^2$
$\Delta Q = Q_{calc} - Q_{obs}$

the unit cell. For this reason it will not be possible to determine fluorine in the natural micas solely by the *c* parameter.

The ideal compositions of phlogopite and fluorophlogopite are given in Table 6. The largest amount of fluorine reported in a natural phlogopite is 6·74% (Jakob and Parga-Pondal, 1932, p. 273). Although this and many other micas having high fluorine contents are generally found in pegmatites, there appears to be no restriction on mode of occurrence.

Table 6. Comparison of ideal composition of phlogopite and fluorophlogopite in weight %

	Phlogopite	Fluorophlogopite
SiO_2	43·19	42·78
Al_2O_3	12·22	12·10
MgO	28·99	28·72
K_2O	11·29	11·18
H_2O	4·31	—
F_2	—	9·02
	100·00	103·80
Correction for F → 0		3·80
		100·00

Geological Applications

Phlogopite in igneous rocks

It is an often-recorded deduction that one of the earliest formed minerals in some magmas is a mica (e.g., biotite). A mica may be found in both high- and low-silico plutonic rocks, but in the extrusive rocks the occurrence of mica is dependent on several conditions. For example, Washington (1896) pointed out that the biotite of the intermediate and basic volcanic rocks is usually altered or transformed into other minerals, whereas the siliceous volcanic rocks exhibit no such decomposition of the mica. Some insight into these field observations may be gained from an examination of the stability curve of phlogopite.

It may be seen from Fig. 10, compiled from the data of Heinrich (1946), that micas close to phlogopite in composition are found predominantly in the ultrabasic igneous rocks and the marbles. The iron-rich biotites appear in those igneous rocks which are believed to be later than the ultrabasics in the accepted rock series. Although it cannot be said with certainty whether iron raises or lowers the upper stability limit of phlogopite, it is most likely that the decomposition will take place at somewhat lower temperatures for a given pressure. This opinion is based on the known melting relations of the olivines and the pryoxenes; however, it must be borne in mind that in these analogues the equilibrium is between crystals and liquid, while the decomposition reaction for the mica involves crystals and vapour. Perhaps the best analogous reaction is the serpentinization of olivine. The equilibrium curve for this reaction is lowered with increasing iron content of the olivine (Bowen and Tuttle, 1949, p. 453; Flaschen and Osborn, 1954). The lowering is about 260°C at all pressures investigated for the pure iron system. Experimental work on the stability relations of annite (the iron-rich member of the biotites, $KFe_3AlSi_3O_{10}(OH)_2$) is now under way. The preliminary data indicate that iron-bearing phlogopites can be grown at temperatures slightly lower than those for pure phlogopite. In addition, two natural iron-bearing phlogopites broke down at approximately the same temperature as synthetic phlogopite; so, with some

confidence one may also apply the stability relations of phlogopite to those rocks containing biotites.

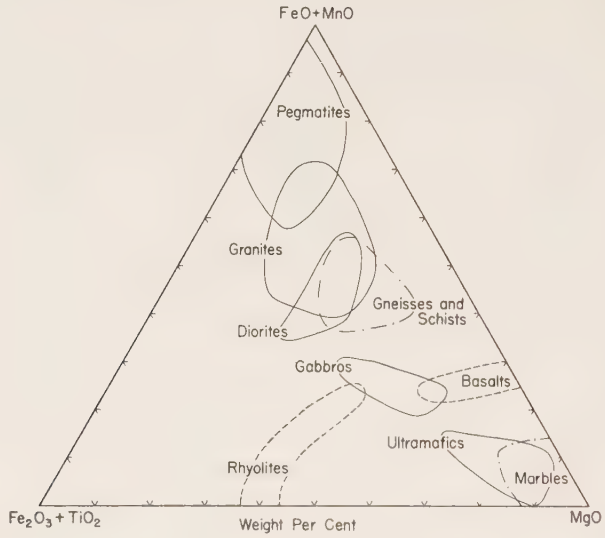

Fig. 10. Variation of chemical composition of biotite with rock type (compiled from diagrams of Heinrich, 1946).

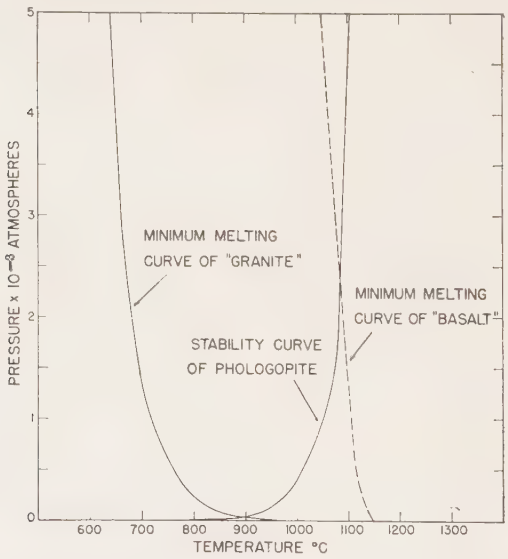

Fig. 11. Relation of upper stability curve of phlogopite to the determined minimum melting curve of granite (Bowen and Tuttle, 1953, p. 50) and the estimated minimum melting curve of basalt.

In Fig. 11 is given the relation of the stability curve of phlogopite to the determined minimum melting curve of granite (Bowen and Tuttle, 1953, p. 50) and an estimate of the melting curve of basalt. The latter is based on an average of the observed extrusion temperature of basalts and on the character of the known

change of melting point with pressure for the system diopside—water (Yoder, 1952a, p. 1318). Although there may be some difference of opinion as to the exact temperatures and pressures of the basalt melting curve and the stability curve of a phlogopite bearing some fluorine and iron, the general relations of the stability curves will not be changed significantly.

First, the relation of the granite and phlogopite curves will be examined. It can be seen that the upper stability limit of phlogopite exceeds the minimum melting curve of granite at all temperatures and pressures except for a small region below approximately 60 atmospheres pressure. It would appear as though a mica should be found on the liquidus surface of the granite system. Such is the case according to Bowen and Tuttle (1953, p. 50), who melted two natural granites under various water vapour pressures and found that biotite was the primary phase of crystallization. The relation of the curves also indicates that, whether the granite is crystallized under deep-seated conditions or is poured out onto the surface, the phlogopite will remain within its stability limits. It is reasonable to assume that a lava could sustain approximately 60 atmospheres water vapour pressure before being quenched at the surface. It is concluded then that a biotitic mica, once it has formed in a siliceous rock, will persist without decomposition whether cooled under deep-seated conditions or quenched at the surface. This conclusion is in accord with the observations of Washington.

The relation of the phlogopite stability curve to the melting curve of a basic rock suggests a somewhat different behaviour than that for the siliceous rocks. The deep-seated basic rocks may also have a mica on the liquidus; but the extrusive equivalents will not, since the upper stability limit of phlogopite lies well below the melting curve of the basic rock in the region of low water vapour pressure. The mica of basic rocks crystallizing at depth will be decomposed if brought to the surface.[1] This is essentially what had been deduced by Washington many years ago. Iddings (1891) also arrived at a similar conclusion in his study of the intrusive rocks of Electric Peak and the pyroclastic rocks of the Sepulchre Mountains in Wyoming. The two rock masses were of identical bulk composition, yet the intrusive rock was a biotite-bearing diorite and the extrusive rock was a pyroxene andesite. Niggli (1912) ascribed this difference in mineralogy of the two rocks to the loss of water from the extrusive rock at the surface. The stability limits of the mica had been exceeded by the drop in pressure at the elevated temperature.

Both the formation and resorption of mica are clearly exhibited in the volcanic rocks of southwest Uganda described by Holmes (1942). In the lavas, leucite-, kalsilite-, and olivine-bearing rocks are found without biotite. The ejected blocks and xenolithic inclusions, however, contain biotite in various stages of resorption. In one lava specimen "the kalsilite merges almost imperceptibly into ragged patches of phlogopitic biotite" where it would otherwise meet olivine (Holmes, 1942, p. 204). It appears that on the slow cooling of the lava the olivine and kalsilite reacted to form a mica. It seems likely that the phlogopite curve was crossed twice—first during the lowering of the pressure on extrusion, and second during the lowering of temperature on cooling.

[1] It is assumed that $P_{H_2O} = P_{total}$ and the water vapour pressure is directly related to the depth.

Larsen, Gonyer, and Irving (1937, p. 900) in their study of the volcanic rocks of the San Juan Region, Colorado, reached the conclusion that "The biotites of the extrusive rocks commonly show resorption and, while the extent of resorption varies greatly in rocks of the same composition, on the average it is greater in the less siliceous rocks, and may be almost entirely lacking in the rhyolites." In addition, they expressed the belief that "The resorption of . . . biotite is favoured by near surface conditions; it may begin before the magma is erupted to the surface, but much of it takes place after eruption." The deductions based on the experimental data are in accord with these conclusions.

The resorption of mica and the subsequent release of potash may account for the potash-rich zone observed around some feldspars.

Phlogopite in sediments

A trioctahedral clay mica has been identified in the soil of Balquhain, Aberdeenshire, Scotland (Walker, 1950). The existence of such a mica was predicted by Hendricks (1942, p. 285) and it was suggested by him that the mineral pholidolite might be a degraded trioctahedral mica equivalent to the dioctahedral illite. It was shown later by Walker (1950, p. 75) that pholidolite was "an aggregate of montmorillonite crystallites pseudomorphous after mica." An examination of the diffuse X-ray pattern and the accompanying table of indexed reflections published by Walker (1950, pp. 74-75) suggests that his material is a 1Md trioctahedral mica. The analogous illite in the dioctahedral micas is defined by Grim as having a 10 Å c spacing (1953, p. 36) and "some randomness in the stacking of the layers in the c direction . . . " (1953, p. 67). It was shown by the writers (Yoder and Eugster, 1953, p. 1496) that the type illite is specifically a 1Md mica, which is in accord with the structural specifications of Grim. It was also demonstrated that 1Md can be gradually transformed by hydrothermal treatment into 1M, that is, from a structure having completely random stacking of units to one having an orderly stacking of units. The small degree of diffuseness in Walker's material suggests that the stacking is in the greater part ordered with only some randomness in the stacking of the units. It is presumed that either the relative loss of order can be interpreted as evidence of the weathering of an original 1M mica, or the relative gain in order, as evidence of the incomplete growth of authigenic 1M mica in the sediment. (On the other hand, the diffuseness in the X-ray pattern may be due, all or in part, to the residual materials resulting from the heat treatment employed by Walker to destroy the kaolinite present in the sample.) The completely disordered phlogopite produced synthetically and its subsequent ordering at higher temperatures (Fig. 8) well illustrate the stages of the process described by Walker. The process may be represented schematically as either 1Md $\rightarrow$ 1M (authigenic growth) or 1M $\rightarrow$ 1Md (weathering). It is likely that a trioctahedral mica having a completely disordered structure (1Md) similar to the low-temperature synthetic product will be found in young soils.

The composition of the material from Scotland as given by the approximate analysis indicates that the mica is, ideally, on the join phlogopite—Mg-montmorillonite, the so-called hydrophlogopites. This is again analogous to the illites which lie on the join muscovite—montmorillonite. More will be said on this point

in a subsequent paper, in connection with the solid solutions found experimentally between 1Md muscovite and 1Md phlogopite. It is well to emphasize that the hydrophlogopites are not structurally equivalent to vermiculite, which is related to the montmorillonites (MATHIESON and WALKER, 1954).

Phlogopite in marbles

A common occurrence of phlogopite is in the metamorphosed impure limestones and dolomites. The question of the growth of mica in these rocks involves the nature of the initial materials in the sediments. The possible reacting materials are limited and not well known. The chief difficulty is in identifying the source of K_2O. Studies on the minor constituents of impure limestones and dolomites by GRIM, LAMAR, and BRADLEY (1937), by FÜCHTBAUER (1950), and by ROBBINS and KELLER (1952) indicate that illite is the dominant clay mineral. It does not appear to be known whether these clay micas are dioctahedral or trioctahedral. One reaction from which phlogopite may result, then, may involve dolomite and 1Md muscovite (= illite). It is likely that a Ca-bearing product, such as zoisite or tremolite, would be formed in addition. The appearance of these reaction products is usually assigned a slightly higher grade of metamorphism. The reaction of illite with chlorite, or its low-temperature equivalent, aluminous serpentine, producing phlogopite is a well-known possibility. Phlogopite could form, of course, directly from a 1Md trioctahedral detrital mica, as demonstrated by the laboratory experiments. This source is not without difficulties since most 1Md micas are usually leached of K_2O on weathering to a Mg-montmorillonite (GRIM, DIETZ, and BRADLEY, 1949, p. 1806). It is also possible that detrital potash feldspar would react with dolomite, but the rate of such a reaction might be dependent on a higher grade of metamorphism. Reactions involving colloids having potassium in the boundary layer of the constituent particles are not improbable. It appears as though a more detailed investigation of the mineralogy of the limestones and dolomites is needed in order to fix the source material from which the necessary K_2O is derived for the formation of phlogopite during metamorphism.

The above-named reactions do not exhaust the possible ways in which phlogopite may appear in a metamorphic rock. Whatever the reaction, it will take place under specific sets of conditions and these will be different for each reaction. It is necessary, therefore, to establish the nature of the reaction before the particular phlogopite isograd can be adequately described. Similarly, the disappearance of phlogopite during metamorphism will be dependent on the nature of the reaction. The experiments fix the maximum conditions of stability of pholgopite, yet there are many reactions which consume phlogopite well below these conditions. In each case the reaction must be specified if the isograd marking the disappearance of phlogopite is to have meaning.

In summary, it is suggested that the experimental work may be applied indirectly to geological problems involving the major rock types. For the igneous rocks an account is given of the formation and resorption of biotite. For the sedimentary rocks a picture of the authigenic growth, or inversely, the weathering of the mica, is outlined. And for the metamorphic rocks, some of the problems

relating to the geochemistry of phlogopite and to its appearance and disappearance during metamorphism are presented.

Acknowledgments

The writers are indebted to the many investigators who have contributed specimens and preparations for the mica studies. Dr. J. V. Smith's co-operation in the crystal structure interpretation and his continued support are gratefully acknowledged. The investigation was aided considerably by the efficient maintenance of the various pieces of apparatus by Mr. John Van den Heurk. The comments and criticism of Drs. S. B. Hendricks, J. V. Smith, and W. S. MacKenzie, and Mr. F. R. Boyd, who critically read the manuscript, are appreciated.

References

Beatty, S. (1949) X-ray spectrometer study of mica powders. Amer. Mineral. **34,** 74–82

Bowen, N. L. (1917) The sodium-potassium nephelites. Amer. J. Sci. **43,** 115–132

Bowen, N. L., and Tuttle, O. F. (1949) The system MgO—SiO_2—H_2O. Bull. Geol. Soc. Amer. **60,** 439–460

Bowen, N. L., and Tuttle, O. F. (1953) Beginning of melting of some natural granites. Carnegie Inst. Wash. Yearbook No. **52,** 50

Bradley, W. F. (1945) Molecular associations between montmorillonite and some polyfunctional organic liquids. J. Amer. Chem. Soc. **67,** 975–981

Federico, M., and Fornaseri, M. (1952) Le miche dei proietti del Vulcano Laziale. Period. Min. Roma **21,** 209–227

Flaschen, S. S., and Osborn, E. F. (1954) The system FeO—SiO_2—H_2O. Amer. Mineral. **39,** 328 (Abs.)

Füchtbauer, H. (1950) Die nichtkarbonatischen Bestandteile des Göttinger Muschelkalkes mit besonderer Berücksichtigung der Mineralneubildungen. Heidelberger Beitr. Min. u. Petr. **2,** 235–254.

Grim, R. E. (1953) Clay Mineralogy (McGraw-Hill Book Co., New York)

Grim, R. E., Dietz, R. S., and Bradley, W. F. (1949) Clay mineral composition of some sediments from the Pacific Ocean off the California coast and the Gulf of California. Bull. Geol. Soc. Amer. **60,** 1785–1808

Grim, R. E., Lamar, J. E., and Bradley, W. F. (1937) The clay minerals in Illinois limestones and dolomites. J. Geol. **45,** 829–843

Heald, M. T. (1950) Structure and petrology of the Lovewell Mountain quadrangle, New Hampshire. Bull. Geol. Soc. Amer. **61,** 43–89

Heinrich, E. W. (1946) Studies in the mica group; the biotite-phlogopite series. Amer. Jour. Sci. **244,** 836–848

Heinrich, E. W. (1952) Natural mica studies. First Ann. Rept. Eng. Res. Inst., Univ. Michigan, Ann Arbor, Michigan, pp. 1–15

Heinrich, E. W. (1953) Natural mica studies. March Quart. Rept. Eng. Res. Inst., Univ. Michigan, Ann Arbor, Michigan, pp. 1–28

Hendricks, S. B. (1939) Random structures of layer minerals as illustrated by cronstedite ($2FeO \cdot Fe_2O_3 \cdot SiO_2 \cdot 2H_2O$). Possible iron content of kaolin. Amer. Mineral. **24,** 529–539

Hendricks, S. B. (1942) Lattice structure of clay minerals and some properties of clays. J. Geol. **50,** 276–290

Hendricks, S. B., and Jefferson, M. E. (1939) Polymorphism of the micas. Amer. Mineral. **24,** 729–771

Hildebrand, F. A. (1953) Minimizing the effects of preferred orientation in X-ray powder diffraction patterns. Amer. Mineral. **38,** 1051–1056

Holmes, A. (1942) A suite of volcanic rocks from south-west Uganda containing kalsilite (a polymorph of $KAlSiO_4$). Mineral. Mag. **26,** 197–217

Iddings, J. R. (1891) The eruptive rocks of Electric Peak and Sepulchre Mountain, Yellowstone National Park. Ann. Rept. U.S. Geol. Surv. **12,** 577–663

Jakob, J., and Parga-Pondal, I. (1932) Beiträge zur chemischen Konstitution der Glimmer, X. Zeit. Kryst. **82,** 271–284

Kunitz, W. (1924) Die Beziehungen zwischen der chemischen Zusammensetzung und den physikalisch-optischen Eigenschaften innerhalb der Glimmergruppe. Neues Jahrb. Min., Beil. Bd. **50,** 365–413

Kunze, G. (1954) Über die rhombische Modifikation von $KAlSiO_4$ in Anlehnung an den Kalsilit. Heidelberger Beitr. Min. u. Petr. **4,** 99–129

Larsen, E. S., and Berman, H. (1934) The microscopic determination of the nonopaque minerals. U.S. Geol. Surv. Bull. **848,** 1–266

Larsen, E. S., Gonyer, F. A., and Irving, J. (1937) Petrologic results of a study of the minerals from the Tertiary volcanic rocks of San Juan Region, Colorado. 6. Biotite. Amer. Mineral. **22,** 898–904

MacDonald, G. J. F. (1953) Anhydrite-gypsum equilibrium relations. Amer. J. Sci. **251,** 886–888

MacEwan, D. M. (1946) The identification and estimation of the montmorillonite group of minerals with special reference to soil clays. J. Soc. Chem. Ind. **65,** 298–305

Mathieson, A. M., and Walker, G. F. (1954) Crystal structure of magnesium-vermiculite. Amer. Mineral. **39,** 231–255

Morey, G. W., and Ingerson, E. (1937) A bomb for use in hydrothermal experimentation. Amer. Mineral. **22,** 1121–1122

Niggli, P. (1912) Die gasförmigen Mineralisatoren im Magma. Geol. Rundschau **3,** 472–482

Robbins, C., and Keller, W. D. (1952) Clay and other non-carbonate minerals in some limestones. J. Sediment. Petrol. **22,** 146–152

Roy, R. (1949) Decomposition and resynthesis of the micas. J. Amer. Ceram. Soc. **32,** 202–209

Schairer, J. F. (1954) The system K_2O—MgO—Al_2O_3—SiO_2: I. Results of quenching experiments on four joints in the tetrahedron cordierite—forsterite—leucite—silica, and on the join cordierite—mullite—potash feldspar. J. Amer. Ceram. Soc., in press.

Smith, J. V., and Yoder, H. S. (1953) Theoretical and X-ray study of the mica polymorphs. Bull. Geol. Soc. Amer. **64,** 1475 (Abs.)

Strese, H., and Hofmann, V. (1941) Synthese von Magnesiumsilikat-Gelen mit zweidimensional regelmässiger Struktur. Zeit. anorg. u. allgem. Chemie **247,** 65–95

Sundius, N., and Byström, A. M. (1953) Decomposition products of muscovite at temperatures between 1000° and 1260°C. Trans. British Ceram. Soc. **52,** 632–642

Tuttle, O. F. (1949) Two pressure vessels for silicate-water studies. Bull. Geol. Soc. Amer. **60,** 1727–1729

Van den Heurk, J. (1953) Improved hydrothermal quenching apparatus. Bull. Geol. Soc. Amer. **54,** 993–996

van Valkenburg, A., and Pike, R. G. (1952) Synthesis of mica. J. Res. Nat. Bur. Stand. **48,** 360–369

Walker, G. F. (1950) Trioctahedral minerals in the soil-clays of north-east Scotland. Mineral. Mag. **29,** 72–84

Washington, H. S. (1896) The magmatic alteration of hornblende and biotite. J. Geol. **4,** 257–282

Winchell, A. N., and Winchell, H. (1951) Elements of Optical Mineralogy, Part II (John Wiley & Sons, Inc., New York)

Yoder, H. S. (1950) High-low quartz inversion up to 10,000 bars. Trans. Amer. Geophys. Union **31,** 827–835

Yoder, H. S. (1952a) Diopside—water system. Bull. Geol. Soc. Amer. **63,** 1318 (Abs.)

Yoder, H. S. (1952b) The MgO—Al_2O_3—SiO_2—H_2O system and the related metamorphic facies. Amer. J. Sci. Bowen Vol., 569–627

Yoder, H. S., and Eugster, H. P. (1953) Syntheses and stability of the muscovites. Bull. Geol. Soc. Amer. **64,** 1496 (Abs.)

Geochimica et Cosmochimica Acta, 1954, Vol. 6, pp. 186 to 196. Pergamon Press Ltd., London

Geochemical implications of the isotopic composition of carbon in ancient rocks

Harmon Craig
Institute for Nuclear Studies, University of Chicago.

(*Received* 10 *July* 1954)

ABSTRACT
The use of the isotopic composition of carbon in ancient rocks as an indication of biologic or inorganic origin is critically discussed in terms of the assumptions that must be made in this procedure. These assumptions actually represent unsolved problems in the geochemistry of carbon which must be investigated; their *a priori* justification is not possible. It is concluded that this method of identification is not valid. The hypothesis that graphite can be formed from limestone, and Rankama's argument that thermodynamic principles are not applicable to natural processes, are discussed.

Introduction

The purpose of this communication is the critical evaluation of present data on the isotopic composition of carbon in Pre-Cambrian shales, slates, schists, gneisses, and marbles. The recent extensive discussion by Rankama (1954a), in which strong exception to various points raised previously by me is taken, emphasizes clearly the basic differences in our understanding and formulation of the various problems involved. Rankama's formulation of the problem of natural variations in the isotopic composition of carbon is built around one specific aim—the application of the isotopic data to determine whether ancient carbonaceous deposits have resulted from organic or inorganic processes. The approach of the present writer has been completely opposite; it is based on the presumption that the data on these ancient rocks must be integrated generally with all the other data and evaluated in terms of basic geological and chemical principles. The integrated data, so evaluated, have broad implications for the fundamental problems of geochemistry, and the aim of this writer has been the development and understanding of these implications for use in such problems. The particular application of the data which Rankama has attempted to develop rests on several very serious assumptions, and it appears, upon serious scrutiny, that these assumptions are in fact just the basic problems of the geochemistry of carbon which we should be trying to solve.

The problem is, moreover, of interest in a broader sense, since Rankama's defence of his procedure involves the challenging of the applicability of thermodynamic principles to geological problems. The implications of the argument thus transcend the subject matter; they involve the whole concept of what the naturalist can know about his physical world, and how he can study it. In the following discussion, the physicochemical problems relevant to the specific problem at hand are discussed in this context.

Statement of the Problem

The argument that carbon in ancient rocks can be uniquely identified, as to origin, by its isotopic composition was first proposed by Wickman (1941); it has since been developed in several papers by Rankama and Wickman dealing with applications to various types of material. The original data on which the premise

was based were those of NIER and GULBRANSEN (1939) and MURPHEY and NIER (1941); more recent and extensive data obtained by this writer (1952, 1953a, 1954a, b) are summarized in Table 1, which shows the range of variation in the various groups of natural material relevant to the following discussion. The numerical values are given in terms of per mil enrichment in C^{13} with respect to the writer's standard, which has the isotopic composition of average marine limestone; i.e., in terms of δ values* which have the advantage that the various enrichment factors can be directly discerned. It is seen from the table that graphitic carbon covers the whole of the 4 per cent range of variation from the "light" organic carbon to the "heavy" carbon in limestones.

RANKAMA's premise is that carbon with a δ value lighter than the arbitrarily chosen value of $-21{\cdot}7$ per mil lies in the "biogenic range," and, in the absence of contradictory geological evidence, "one is safe to conclude" that carbon in shales, slates, and schists with such a composition is of biological origin (1954a, p. 150). This argument was originally applied by him (1948) to a group of Pre-Cambrian carbonaceous materials, including some small carbonaceous accumulations in Archean slates which had been named *Corycium* by SEDERHOLM in the belief that they represented carbon derived from primitive plants. The conclusion reached by

Table 1. *Isotopic composition of carbon in various types of natural occurrences* (CRAIG, 1952, 1953a, 1954a, b)

Source material	δC^{13} (per mil)
Marine limestones	$+2{\cdot}4$ to $-3{\cdot}3$
Recent shells	$+1{\cdot}9$ to $-3{\cdot}8$
Atlantic Ocean bicarbonate	$-1{\cdot}3$ to -2.9
Atmospheric CO_2	$-7{\cdot}4$ to -9.9
Marine plants and animals	$-8{\cdot}1$ to $-17{\cdot}9$
Normal terrestrial plants	-21.1 to $-32{\cdot}1$
Fossil wood	$-22{\cdot}4$ to $-27{\cdot}3$
Coal	$-21{\cdot}6$ to $-27{\cdot}2$
Paleozoic and younger marine shales and slates	$-26{\cdot}1$ to $-30{\cdot}8$
Petroleum	$-23{\cdot}0$ to $-29{\cdot}4$
Huronian shales and slate	$-28{\cdot}5$ to $-30{\cdot}7$
Pre-Cambrian schists	$-9{\cdot}8$ to $-35{\cdot}5$
Graphite from gneisses, pegmatites, marbles	$-2{\cdot}7$ to $-19{\cdot}7$
Igneous rocks	$-19{\cdot}0$ to $-26{\cdot}0$

RANKAMA was that the isotopic data furnished "final proof of the organic nature of the *Corycium* . . . the oldest [fossil] ever recorded with definite certainty." In the same paper he concluded that all but one of his other samples were also of organic origin; the one, being as rich in C^{13} as limestones, was interpreted as being graphite derived from limestone, in stated agreement with its occurrence at the contact of a pegmatite vein intersecting limestone.

* δ in per mil $= \left[\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}}\right] \times 1000$, where R is the ratio C^{13}/C^{12}.

Wickman and von Ubisch (1952) also reasoned that graphite derived from carbonate deposits should have an isotopic composition close to that of the carbonate and greatly different from organic material, and thus decided that a certain graphite deposit was not of organic origin.

The arguments of Rankama and Wickman cited above were based entirely on comparison of the isotopic composition of the various samples investigated with the ranges of isotopic composition of limestones and material of known organic origin, as shown in Table 1. No discussion of the underlying premises on which such arguments must be based, or of the physicochemical principles involved in these unstated assumptions, was given. However, in reply to briefly stated criticisms (Craig, 1953a, b), Rankama (1954a) has discussed the various points involved at some length with vigorous reaffirmation of the validity of the procedure; the following sections contain a discussion of Rankama's interesting treatment of the various principles which form the basis of my dissent.

Isotopic Fractionation in the Formation of Graphite

Previously (1953a, b), I pointed out that the isotopic identification of graphite as of biologic or limestone origin rests on the tacit assumption that there is no mechanism by which light graphite can be formed from heavy carbonate carbon, or heavy graphite from light organic carbon. We are not able to calculate the equilibrium fractionation factors between graphite and other carbon compounds; moreover, even if we knew these factors and the compounds involved, we could not be sure that the process took place under equilibrium conditions where the factors would apply; thus this assumption cannot be made. In reply to this criticism, Rankama (1954a, p. 149) agreed that we have no knowledge of whether equilibrium conditions obtained, and then stated "The tacit assumption relative to the formation of light and heavy graphite consequently cannot be disqualified."

This statement amounts to saying that one cannot prove that Rankama is wrong; in precisely the same way, one cannot prove that any completely ad hoc assumption is incorrect when no data exist to test the validity of the assumption. The point is that any number of such ad hoc postulates can be made; science, however, accepts only postulates based on some positive foundation, or it ceases to be science. The burden is upon Rankama and Wickman to show that carbon with such and such an isotopic composition cannot be produced in any other way than the one they specify, otherwise the isotopic evidence is meaningless.

In actual fact this "crossing over" of ranges is certainly possible—the isotopes of the light elements are known to be fractionated in both equilibrium and rate processes, which, after all, accounts for the fact that isotopic variations are found in nature at all. The fractionation factors cannot be calculated for graphite reactions and so one simply cannot make the assumption to which I object. Moreover, it seems likely that rate processes would govern the isotopic fractionation in many cases; in such instances the lighter isotope generally reacts more rapidly and one can readily expect that, e.g., carbon produced by reduction of CO_2 of limestone composition might be very much lighter than the original limestone if total conversion to graphite is not obtained. Large enrichment factors are encountered in such processes and the resultant carbon could easily fall in the biogenic range.

Rankama (1948) concluded that graphitization of organic carbon causes an enrichment in C^{13}; this statement was based on the fact that half of the schist carbon samples whose origin he was attempting to determine were too rich in C^{13} to fall in what he delimits as the "biogenic range." The same reasoning is applied in his most recent work (1954b, c) where two out of five samples which fall out of the organic range are yet deduced to be of organic origin. In his discussion (1954a), Rankama restates his conclusion that graphitization of organic material causes an enrichment in C^{13} (p. 144), yet he states in the same paper that "the available evidence indicates that light carbon does not grow heavier during graphitization" (p. 149). Apparently Rankama would like to have organic carbon become a little heavier to support his argument (1950, p. 77) that the lightest value must be used as the mean, yet not heavy enough to ever allow organically derived carbon to approach limestone carbon in isotopic composition. These points are discussed farther on in connection with the problem of the Pre-Cambrian exchange reservoir.

Thermodynamics in Nature and the Laboratory

In the preceding section the isotopic phenomena were discussed on the assumption that appropriate chemical mechanisms were available to produce graphite from the sources that Rankama and Wickman wish to distinguish. Actually, as I pointed out previously (1953a, p. 85), carbon dioxide is stable over the whole range of metamorphic temperatures unless some reducing element is available; that is, it cannot by itself dissociate to produce graphite. The equilibrium constants for dissociation of CO_2 at 1000°K are as follows:

$$CO_2 = C + O_2 \qquad K = 2 \times 10^{-21}$$

$$CO_2 = CO + \tfrac{1}{2}O_2 \qquad K = 6 \times 10^{-11}$$

with both constants decreasing below this temperature. Carbon dioxide might be reduced by metallic iron or hydrogen, but the above data show that graphite cannot be produced by simply heating limestone to the temperatures obtained in metamorphic processes.

Rankama (1954a, pp. 149–150) objects to this observation with the statement that the formation of graphite by reduction of CO_2 in a silica tube at 2–3 atm. and 700–1100°C, was observed by Frauenfelder in 1924. Rankama states that experiments were done with an excess of oxygen present to insure that the reaction went via the first equation given above, and that the formation of graphite was ascribed to the *action of silica as a catalyst*. He concludes, "It is not too difficult to visualize the formation of graphite at igneous contacts in limestone bodies by the reduction of carbon dioxide. With all due respect to the dissociation constants introduced by Craig, it appears that one here has another case in point to indicate that Nature does not always obey the rules set up for her guidance in the laboratory."

From the above statements, it would seem that Rankama believes that a catalyst can shift the equilibrium position of a chemical reaction, or that the modus operandi of a catalyst differs in nature and in the laboratory. It is well known, however, that catalysts do not shift chemical equilibrium but merely change the rate of reaction, affecting both the direct and reverse reactions to the

same extent. A catalyst merely provides a locus where the activated state necessary for the reaction can be achieved with a lower expenditure of free energy; it is experimentally observed that catalysts do not affect the final equilibrium position, but only change the time necessary to reach equilibrium. The reaction can only go in the direction of the equilibrium position indicated by the thermodynamic data; whether equilibrium is actually reached or not does not matter since the equilibrium constants cited above show that CO_2 will not be dissociated at such temperatures. Note that the first reaction shown is pressure independent and in the second, higher pressures favour the stability of CO_2. The various reactions of carbon and oxygen are so well known that it is obvious that the experiment cited by RANKAMA is in complete conflict with all other experimental data on the subject.

If, on the other hand, RANKAMA believes that a catalyst operates differently in nature than in the laboratory, his view, if accepted, would indeed have serious implications for science. It is easily shown that the shifting of chemical equilibrium by a catalyst would be a violation of the second law of thermodynamics. The laws of nature are discovered, not decreed, by scientists. If, as RANKAMA states, nature does not obey the laws discovered in the laboratories, we could not today know a single physical constant, and instead of an organized body of knowledge, science would be chaos. The point, of course, is that the laboratory is itself a part of nature—there are, in principle, no natural processes which cannot be duplicated in the laboratory. The rates of certain processes may be far too slow to reach equilibrium in the time available for observation, but given the thermodynamic data we can calculate the final equilibrium position and thus the direction in which the reaction will proceed.

It is interesting to note that RANKAMA (1954a, p. 145) also accepts the "cyclical enrichment" process postulated by WICKMAN (1952) to account for the enrichment of C^{12} in terrestrial plants, and the postulated lack of such a process to account for the anomalous lack of such enrichment in some cases. I have shown, in the paper repeatedly cited by RANKAMA (CRAIG, 1954b), that this mechanism is also a direct violation of basic physicochemical principles. "With all due respect" to RANKAMA's "dynamic reasoning," it would seem that some attempt should be made to formulate these problems in terms of the fundamental concepts embodied in all the scientific disciplines.

With respect to the graphite problem, it is clear that only under very special circumstances can graphite be formed from limestone carbon alone, i.e., when some reducing agent such as juvenile hydrogen or metallic iron may have been present; in neither of the graphite samples investigated by RANKAMA and WICKMAN which were concluded to have originated from limestone does it appear that such conditions could have been fulfilled. In general, the most probable source for graphite is organic material. When organic material, calcium carbonate, and water are heated together, a variety of reactions involving C, CO, CO_2, CH_4, H_2O, H_2, will occur, and the isotopic composition of the resultant graphite will be dependent on a great many factors: temperature, the degree to which the various equilibria obtain, the relative amounts of organic matter and carbonate, and the amount of isotopic exchange between the various carbon compounds and any great bulk of

carbonate present. Thus limestone can certainly affect the isotopic composition of graphite by *interaction* with organic material, but it cannot be considered as a general *source* from which graphite has been formed. The identification of graphite of limestone origin by means of its isotopic composition therefore fails on a priori grounds, regardless of the further difficulties discussed in the previous section.

Variations in the Surface Reservoir of Carbon

There is a third assumption, basic to the isotopic identification of ancient carbon, for which any attempted justification comes dangerously close to circular reasoning, namely the constancy, during the course of geologic time, of the mean isotopic composition of the active mixed reservoir of carbon (ocean-atmosphere). If the mean isotopic composition of this reservoir, from which limestone and organic carbon are derived, has been changing with time, the genetic classification of ancient carbon deposits is of course not possible unless allowance can be made for such an effect.

In discussing the isotopic composition of ancient organisms, Rankama (1954a, p. 143) cites my conclusion that the available data indicated no variation since early Paleozoic time; he then states: "Because there is no fundamental dividing line at the outset of the Paleozoic, application of the uniformitarian principle extends Craig's conclusions with equal strength far back into the Pre-Cambrian." This application of the classical principle of geology is incorrect; the principle of uniformitarianism deals only with processes and says nothing at all about the isotopic or chemical composition of any part of the earth or the earth as a whole. In fact, there is a fundamental dividing line at the Pre-Cambrian–Paleozoic break, namely the lack, in Pre-Cambrian deposits, of any material which has definitely preserved its isotopic composition from the time of formation, and which is directly comparable to some more recent type of material such as coal or wood.

In this section we shall discuss only the possible variation in the surface reservoir as it affects the isotopic composition of organic carbon deposited in shale and inorganic carbon in limestone; the possibility of direct sedimentary incorporation of primordial inorganic carbon is discussed in the final section. The constancy of the isotopic composition of the ocean-atmosphere exchange reservoir depends on (1) the amount and isotopic composition of the original carbon present on the surface of the newly formed earth—both unknown at present, (2) the rate of addition of juvenile carbon to the surface of the earth and the isotopic composition of this carbon—both unknown, and (3) the relative rates of deposition of limestone and organic carbon in each geological period—which can probably be estimated. These questions have important applications to the fundamental geochemical problems of the origin of the ocean and atmosphere; they are subject to investigation rather than assumption. The problem of isotopic identification of juvenile carbon and water, and of the constancy of the isotopic reservoir of these substances, is currently under investigation and will be discussed in detail in a future communication. The approach to the problem demands the integration of analytical data on likely sources of juvenile material with the data on the surface accumulations of the elements in question, and, in the case of carbon, the treatment of the data

on the carbon deposited in the sediments must be made along lines somewhat as follows.

It is certainly true that we can find carbon of biologic origin in shales, slates, and schists of Paleozoic and younger age—these are sedimentary rocks, in some cases graptolitic, and we assume with a good deal of confidence that this carbon is derived from the bodies of marine organisms, with, in some cases, some terrestrial plant material also having been supplied. This carbon, and petroleum carbon, is lighter than the carbon in present day marine plants and animals (See Table 1). Since Carboniferous coal has the same composition as Tertiary lignites, Pleistocene peat and wood, and Recent wood, and since the sediments examined range from Cambrian to Eocene with no trend in isotopic composition, we infer that the marine organisms of the Paleozoic had the same isotopic composition as present day organisms, and that in the process by which carbon was concentrated in these sedimentary rocks to its present form, the C^{13}/C^{12} ratio was changed (CRAIG, 1953a). It thus seems reasonable to assume that the surface reservoir composition has not changed appreciably since the early Paleozoic; this time span, however, represents only some 10 per cent of geologic time and thus does not tell us anything about the possible magnitude of the total change in the reservoir during the history of the earth.

The Pre-Cambrian meta-sediments, which are comparable, facies for facies, to younger rocks, include carbon bearing slates and schists. Excluding momentarily any contribution from primordial carbon (cf. below), we do not know any other probable source for the carbon in these rocks than marine organisms, especially when the problem of reducing calcium carbonate, as discussed in the previous section, is properly understood. The presence of what appear to be algal reef structures in Huronian rocks, and the recent discovery of actual algal and fungoid remains in Huronian sediments by TYLER and BARGHOORN (1954), show that living organisms were certainly present in the Huronian seas, and thus we can fairly assume that carbon in the late Pre-Cambrian sediments is almost certainly organic in origin. Since the isotopic composition of carbon in Huronian shales and slates is roughly the same as that of carbon in Paleozoic sediments (Table 1), it is not unreasonable to make the further assumption, as a working hypothesis, that the surface reservoir has been constant since Huronian time, some 10^9 years ago, and that the carbon in these rocks has undergone the same fractionation processes after deposition and during concentration as the marine carbon in younger sediments.

On this basis, the following picture of carbon in ancient rocks can be tentatively drawn. The carbon is presumed to be of organic origin, derived from marine plants and animals, and limestone is not considered to be a source. The light carbon found in slates and schists is believed to be directly comparable to the carbon in the black shales of the Paleozoic and later eras; that is, it represents carbon initially deposited with the same isotopic composition as that of present day marine organisms (the exchange reservoir having the same composition as it has today), and enriched in C^{12} during diagenesis in the same way as carbon in younger shales. This carbon has then later become graphitic with little or no change in isotopic composition.

The heavier carbon, found mainly in gneisses, pegmatites, and marbles, but also in schists, and even in schists occurring in the same areas as schists with light carbon (cf. Table 1; CRAIG, 1953a, p. 83; and data in RANKAMA, 1954a and earlier papers), may represent the result of either or both of the following effects:

1. The carbon was not deposited under the reducing conditions of the black shale environment, and thus has not become enriched in C^{12} during diagenesis (the organic carbon fixed in a metamorphosed Cretaceous chalk may be an example —see CRAIG, 1953a, p. 78), or

2. The carbon, in some cases enriched in C^{12} with respect to its initial composition, was enriched in C^{13} by interaction with limestone carbon during a heating process involving organic material, limestone, and water, as discussed in the previous section.

This formulation seems to be in accord with the present data and with the basic concepts, both geological and chemical, which must be considered, as far as extension back to Huronian time. However, it must be emphasized that the data are extremely scanty, and a change in the composition of the reservoir of perhaps 5 per mil or even more could not be excluded with any certainty. The tendency of the heavier carbon to occur in the stated deposits is in accord with the two mechanisms outlined to account for its composition, but it would be difficult to evaluate the relative contribution of either mechanism to any specific occurrence with any certainty. This outline can only be accepted as a tentative working hypothesis, subject to modification as more detailed data are accumulated—but it is the type of working hypothesis necessary for evaluation of the general problems mentioned at the beginning of this section.

Whether or not the hypothesis is acceptable, the discussion in the previous paragraphs shows that the whole interpretation of the isotopic composition of carbon in ancient rocks is based on the assumption that this is organic carbon, deposited under conditions similar to those of later eras. The further deduction, that since the surface reservoir appears to have been constant, the isotopic composition of the carbon proves its organic origin, must be dismissed as purely circular reasoning. RANKAMA does not, in fact, justify his assumption that the surface reservoir has been constant in the manner outlined above, yet this is the only way that the assumption—so necessary for his argument—can be justified.

THE ISOTOPIC COMPOSITION OF PRIMEVAL SURFACE CARBON

The above picture, tentatively formulated for Huronian and younger deposits, cannot be extended with any justification back to Archean times; the time span is too great and the problem of the possible incorporation in various deposits of the primeval inorganic carbon present on the surface of the earth becomes more and more important as we go backward in time. RANKAMA states that, because of lack of evidence, this latter problem is academic—he would prefer that discussion of the point "be relegated to limbo" (1954b, p. 16). Since it is obvious that there must have existed some inorganic carbon pool from which the carbon required for growth could be drawn by living organisms, RANKAMA's isotopic identification of ancient carbon is absolutely dependent on the assumption that the primeval inorganic carbon did not have an isotopic composition in the biogenic range, or,

more generally, that carbon which may have been supplied to the early sediments from this source did not fall in the biogenic range either inherently or due to fractionation in some inorganic deposition process.

Boato (1954) has found that carbon in meteorites ranges from −3·7 to −18·8 per mil in the meteorites most rich in carbon and water (carbonaceous chondrites) and that ordinary chondrites have carbon of about −25 per mil, that is, the same as carbon in igneous rocks (cf. Table 1). His data indicate that in a process by which some carbon and water are removed from this material, the carbon becomes enriched in C^{12}. The carbonaceous chondrites contain organic compounds of non-biologic origin and thus the enrichment process may be comparable to that which has affected the carbon in Paleozoic black shales. Other hypotheses to account for Boato's observations cannot be excluded, however, on the basis of our present knowledge about these stones. The data on ordinary chondrites are in agreement with those of Murphey and Nier (1941).

The mean composition of the total carbon deposited in the sediments is enriched in C^{13} with respect to carbon in ordinary chondrites and igneous rocks, as was first calculated by Hutchinson (1949); my data indicate a probable value for this mean surface carbon of about −12 per mil (Craig, 1953, p. 87). Hutchinson (op. cit.) and Rankama (1950) have discussed the comparison of the Archean carbon of *Corycium* with this surface mean, on the basis of assuming that the original surface carbon had the isotopic composition of the mean sedimentary carbon. I do not see how one can exclude the possibility that the primeval carbon had the composition of the carbon in chondrites and igneous rocks, thus falling in the biogenic range, and that subsequently juvenile carbon of −12 per mil composition flushed the surface exchange reservoir to a composition from which carbon of −12 per mil composition on the average has been deposited in the sediments ever since. Lacking some known source of organic carbon or some unreplaced limestone carbon from early Archean time, there is no way, with our present knowledge, to tell how far back in time the exchange reservoir has been constant, or to exclude the deposition of light inorganic carbon in Archean sediments, especially when chondritic and igneous rock carbon represent possible sources of such light carbon. The arbitrary assumption that the original carbon on the surface of the earth had the same isotopic composition as the mean carbon deposited in the sediments over all geologic time presumes an extremely special case and is not justifiable on the basis of any present evidence.

With special reference to *Corycium*, it is interesting to note that two analyses of one sample gave values of −14·5 and −26·4 per mil as expressed with respect to this writer's standard, while a second sample analyzed −33·8 per mil (Rankama, 1948). Rankama, in a vigorous criticism of the discussion by Hutchinson (1949), stated that since he had concluded that graphitization tended to enrich organic carbon in C^{13}, the lightest analysis of *Corycium* should be the decisive value (1950, p. 77). As noted in an earlier section, this conclusion was based on the fact that half of the schists analyzed gave values more enriched in C^{13} than his present lower limit for the "biogenic range" (−21·7 per mil) and the then known lower limit for bituminous sediments (Rankama, 1948, p. 414). That is, assuming that the composition of the lightest schist carbon samples proves their organic origin,

the heavier samples are presumed to represent organic carbon which has become enriched in C^{13}. But I do not see how one knows, a priori, that the lightest samples are to be chosen as giving the unchanged composition, unless one assumes to begin with that the carbon is organic in origin and that the surface reservoir has not changed during geologic time. Without these latter assumptions, it would be just as logical to choose the heavy samples as unaltered and deduce that carbon becomes lighter during graphitization. This seems to be another example of circular reasoning in which an original unstated assumption is lifted to the realm of proof by its bootstraps.

Indeed, there is actually some indication that the heaviest value for *Corycium* should be chosen. Rankama absorbed the carbon dioxide resulting from combustion of these samples in barium hydroxide, and the resultant barium carbonate represented yields ranging from only 1·5 per cent to 9 per cent of the amount which should have been collected (1948, p. 406). Experiments by the writer (1953, p. 71–72), and by Baertschi (1952), have shown that barium carbonate absorbed in this way can be as much as 15 per mil too light due to preferential absorption of C^{12}, and that it is thus necessary to get close to total yields to avoid such fractionation. On these grounds, considering the small yields obtained, it may be that the heaviest values are actually the correct ones; in any case it is very difficult to make a case for C^{13} enrichment due to graphitization from the above data, especially since more recent data cited by Rankama (1954a) do not support such an effect.

Conclusions

The thesis of Rankama and Wickman—that carbonaceous deposits can be identified, as to whether the carbon has been derived from organic material or from limestone, by means of the carbon isotopic composition—rests first of all on the assumption that graphite can be formed from limestone and that the identification problem thus exists. It depends secondly on the assumption that in the process of making graphite from these two sources, isotopic fractionation or exchange processes cannot cause carbon from either source to "cross over" the isotopic dividing line which delimits the "biogenic range," and finally on the assumption that the isotopic composition represented by this dividing line has been constant during all of geologic time. The thermodynamic data on the dissociation of carbon dioxide show that rarely, if ever, has graphite been produced from limestone—the lack of adequate reducing substances relegates this origin to very rare and special cases. The assumption that isotopic fractionation or exchange cannot produce a significant change in isotopic composition during graphitization is ad hoc and unjustified. There is no independent evidence that the exchange reservoir composition and the isotopic "dividing line" have been constant during all of geologic time, and constancy of the exchange reservoir composition in Pre-Cambrian time can only be justified by assuming that the carbon in question is of organic origin and has undergone the same processes as carbon in younger rocks of the same facies. This assumption may be justified for Huronian sediments but becomes more and more difficult to justify as we go back in time.

The actual identification problem is the question of distinguishing organic carbon from possible primeval inorganic carbon in Archean rocks. Rankama's

premise here rests on the assumption that such primeval carbon did not, inherently, lie in the "biogenic range," or that carbon derived from the primeval inorganic pool could not have been deposited with "biogenic" composition by inorganic fractionation processes. Since carbon in igneous rocks and in chondritic meteorites falls in the "biogenic range," since the composition of the surface exchange reservoir in Archean time is not known, and since such fractionation processes cannot be ruled out, this assumption cannot be justified. The choice of the lightest of a series of carbon samples as the decisive composition for comparison with carbon of known origin can only be justified by circular reasoning. In the case of *Corycium*, it rests also on doubtful analytical data.

Rankama's procedure has been to make some very general assumptions which imply a great deal more than we know about a great many complex factors, and to apply then the consequences of these assumptions to a very particular aspect of the carbon problem. The present writer considers the isotopic identification of ancient carbon samples to be invalid; he believes that we must use the data and our knowledge of geological and chemical principles to investigate the geochemical problems which can be attacked by the techniques of "natural" isotopic tracer methods. These methods give every indication of being as important for geology as the laboratory tracer techniques have been for chemistry and biology, but their use must be governed by the understanding of both the geologic problems and the physicochemical principles involved. Rankama's statement (1954a, p. 151) that "There is a profound difference between the closed systems investigated in a laboratory and the open systems, generally devoid of equilibrium, that exist in Nature" is simply not true; the laws of nature apply in both cases and it is simply up to the earth scientist to be profound enough to reason from the one to the other along the lines of established scientific principles.

References

Baertschi, P. (1952) Helv. Chim. Acta **35,** 1030
Boato, G. (1954) Geochim. et Cosmochim. Acta (in press)
Craig, H. (1952) Anal. Chem. **24,** 604
Craig, H. (1953a) Geochim. et Cosmochim. Acta **3,** 53
Craig, H. (1953b) Econ. Geol. **48,** 600
Craig, H. (1954a) Science **119,** 141
Craig, H. (1954b) J. Geology **62,** 115
Hutchinson, G. E. (1949) Amer. J. Sci. **247,** 27
Murphey, B. F., and Nier, A. O. (1941) Phys. Rev. **59,** 771
Nier, A. O., and Gulbransen, E. A. (1939) J. Amer. Chem. Soc. **61,** 697
Rankama, K. (1948) Bull. Geol. Soc. Amer. **59,** 389
Rankama, K. (1950) J. Geology **58,** 75
Rankama, K. (1954a) Geochim. et Cosmochim. Acta **5,** 142
Rankama, K. (1954b) Compt. rend. Soc. géol. Finlande **27,** 5
Rankama, K. (1954c) Science **119,** 506
Tyler, S. A., and Barghoorn, E. S. (1954) Science **119,** 606
Wickman, F. E. (1941) Geol. Fören. i Stockholm Förh. **63,** 419
Wickman, F. E. (1952) Geochim. et Cosmochim. Acta **2,** 243
Wickman, F. E., and von Ubisch, H. (1952) Geochim. et Cosmochim. Acta **1,** 253

Geochimica et Cosmochimica Acta, 1954, Vol. 6, pp. 197 to 207. Pergamon Press Ltd. London

A theoretical study of alpha star populations in loaded nuclear emulsions*

F. E. Senftle, T. A. Farley, and L. R. Stieff
U.S. Geological Survey, Washington, D.C.

(*Received* 3 *February* 1954)

ABSTRACT

This theoretical study of the alpha star populations in loaded emulsions was undertaken in an effort to find a quantitative method for the analysis of less than microgram amounts of thorium in the presence of larger amounts of uranium. Analytical expressions for each type of star from each of the significantly contributing members of the uranium and thorium series as well as summation formulas for the whole series have been computed. The analysis for thorium may be made by determining the abundance of five-branched stars in a loaded nuclear emulsion and comparing of observed and predicted star populations. The comparison may also be used to check the half-lives of several members of the uranium and thorium series.

Introduction

Loaded nuclear emulsions have been frequently used to observe the successive alpha particles emitted in the radioactive decay of the uranium and thorium series. When the intermediate members of a series are short-lived, stars consisting of two to five alpha tracks will be formed. Yagoda (1949) has shown experimentally that the number of stars with a given number of tracks vary depending on the radioactive series, concentration, and the length of the exposure time. For equal amounts of thorium and uranium, the thorium series forms the most five-branched stars, since the half-lives of the decay products of the thorium series are in general shorter than those of the uranium series. Yagoda (1949) has proposed star counting as the basis of a method for thorium analysis.

This theoretical study of alpha star populations in loaded emulsions was undertaken in an effort to find a quantitative method for the analysis of less than microgram amounts of thorium in the presence of larger amounts of uranium. Frota-Pessôa (1952) has proposed star counting as a method to measure Ra^{226} in the presence of thorium. Isaac and Picciotto (1953) have used a similar method for Th^{230} (ionium) analysis in deep-sea sediments with considerable success, and Schneider and Matitsch (1952) have used the same technique for actinium analysis.

For these and other applications of loaded nuclear emulsions in the quantitative analysis of radioactive isotopes of the thorium or uranium series, a knowledge of the distribution of various multiple-branched stars for a given concentration and exposure time is desirable. Flamant (1948) has calculated the probability of formation of multiple track stars from significant emitters in a series in equilibrium relative to the number of disintegrations of the parent element in each of the natural radioactive series. However, as the parent elements of each series are decaying at different rates, the results do not allow comparison of numbers of like stars from the different series.

The present results permit the calculation of the star type distribution from isolated members of the radioactive series as well as the star type distribution for

* Publication authorized by the Director, U.S. Geological Survey.

the entire series. Flamant's probabilities, calculated for a series in equilibrium, were not intended to represent the star distribution of isolated short half-lived members of a series, as the number of disintegrations of such an emitter originally present is not equal to the number of disintegrations of the parent element of the series.

Method of Calculation

Consider a hypothetical radioactive chain in which each member is in secular equilibrium, and in which the number of atoms, N, of each species is genetically related as follows :

$$N_1\lambda_1 = N_2\lambda_2 = N_3\lambda_3 \ldots N_n\lambda_n$$

The transformations of each member of this series during a time, t, can be represented as in Fig. 1. Of the original number of parent atoms, N_1 (column 1), some

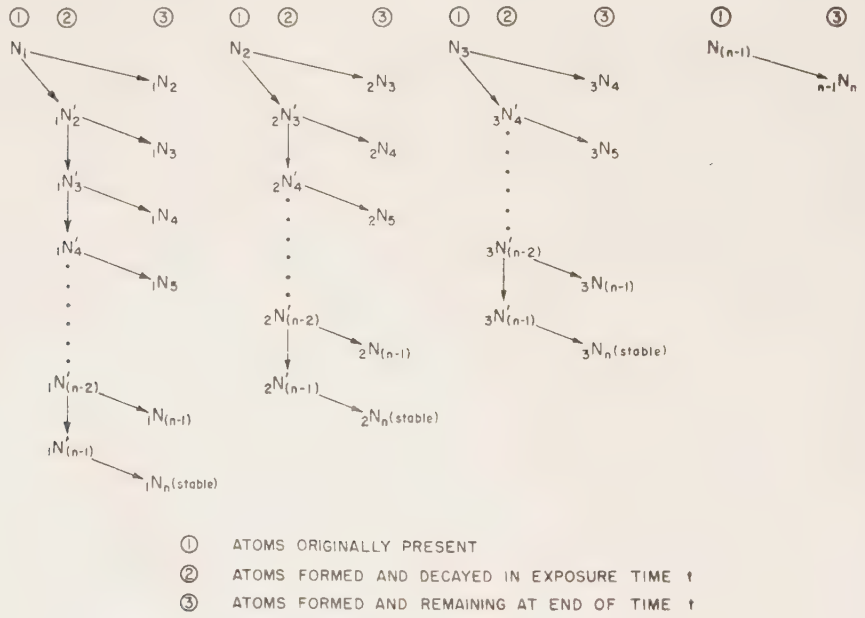

Fig. 1. Schematic diagram of the radioactive transformations of each member of a radioactive series during the time, t.

will decay in time t to form ${}_1N_2$ of type-2 atoms (column 3). During the same period ${}_1N'_2$ type-2 atoms (column 2) will also be formed by decay of the parent species, N_1, but these will further decay to other daughter products, ${}_1N_3$, ${}_1N_4$, etc., before the end of time t. In a similar manner the number of type-2 atoms, N_2, originally present will decay, forming a number of different daughter nuclides, ${}_2N_3$, ${}_2N_4$, etc.

If, for simplicity, we assume that all of the species are alpha emitters, then the number of multiple track alpha stars can be readily deduced. Thus the number of single tracks, ${}_1S_1$, from type-1 atoms will be ${}_1N_2$. Likewise the single tracks,

${}_{1}S_{2}$, accruing from type-2 atoms will be ${}_{2}N_{3}$, and the single tracks formed by the series will be

$$ {}_{1}S = \sum_{\substack{j=n \\ j-2 \\ i=1}}^{i=n-1} {}_{i}N_{j} = {}_{1}N_{2} + {}_{2}N_{3} + {}_{3}N_{4} \cdots {}_{n-1}N_{n} $$

In an analogous manner the number of double-track stars from type-1 atoms will be ${}_{1}N_{3}$ and the series equation will be

$$ {}_{II}S = \sum_{\substack{j=3 \\ i=1}}^{\substack{i=n-2 \\ j=n}} {}_{i}N_{j} $$

However, the natural radioactive series are made up of beta emitters as well as alpha emitters, and the above treatment becomes more complicated because beta particles are not ordinarily observed on alpha sensitive emulsions. Because of these beta emitters a triple alpha-track star, for example, may be formed by a series of decays only three of which are alpha decays. Thus, in the thorium series the total number of triple tracks from Ra^{228} will not be simply represented by the number of Pb^{212} atoms formed but by the sum of the Pb^{212}, Bi^{212}, and Po^{212} atoms, i.e., by

$$ {}_{Ra^{224}}N_{Pb^{212}} + {}_{Ra^{224}}N_{Bi^{212}} + {}_{Ra^{224}}N_{Po^{212}} $$

Bateman (1910) has given an equation for calculating the number of atoms which decay to and remain at any given member of any series during exposure period t. The use of conventional exponential tables may subject the results of the equation to large errors. To obviate such errors in these instances a series expansion method has been used. Tables compiled by Flanagan and Senftle (1954) have been used to facilitate the laborious calculations. The results and calculations presented here have been obtained by the use of the data in this paper. The formulae in Table 1 are based on the amounts of each daughter nuclide that is in equilibrium with one microgram of U^{238}, U^{235}, or Th^{232}. Modes of decay that give rise to an insignificant number of stars during an exposure time up 500 hours, as compared with other emitters in the series, have been ignored both in the individual and in the summation formulae. Terms in the individual formulae, small in comparison with terms in other individual formulae, have been dropped from the summation formulae.

Analytical expressions for calculating the number of multiple tracks from the significant members of each of the naturally radioactive series are shown in Table 1. The exposure time t is in seconds. The summation formulae for each of the series are shown in Table 2. Figs. 2 to 6 show the total track populations for exposure time of up to 500 hours for one microgram of U^{238}, Th^{232}, or 1/139 microgram of U^{235} in equilibrium with their daughter products. When the parent element is in amounts larger or smaller than one microgram, the predicted population for a given multiple star will be directly proportional to the data in the graphs. The ratio of different star types of a given series, on the other hand, is independent of the amount of parent present. For chemically separated radioelements loaded into an emulsion, the star population distribution can be computed from the formulae in Table 1.

Table 1. *Individual emitter star formulae for each series*

I. Thorium^{232} series

A. *Single-track stars*

$$_{\mathrm{I}}S_{\mathrm{Th}^{232}} = 4{\cdot}10_0 \times 10^{-3}\,t$$

$$_{\mathrm{I}}S_{\mathrm{Ra}^{228}} = 2{\cdot}60_1 \times 10^3\,e^{-\lambda_{\mathrm{Ra}^{228}}t} - 2{\cdot}61_1 \times 10^3\,e^{-\lambda_{\mathrm{Th}^{228}}t} + 1{\cdot}1 \times 10e^{-\lambda_{\mathrm{Ra}^{224}}}$$

$$_{\mathrm{I}}S_{\mathrm{Th}^{228}} = 1{\cdot}870 \times 10^3 - 2{\cdot}16_2 \times 10^{-5}\,t - 1{\cdot}87_0 \times 10^3\,e^{-\lambda_{\mathrm{Ra}^{224}}t}$$

$$_{\mathrm{I}}S_{\mathrm{Pb}^{212}} = 2{\cdot}26 \times 10^2 - 2{\cdot}51 \times 10^2\,e^{-\lambda_{\mathrm{Pb}^{212}}t} + 2{\cdot}5 \times 10\,e^{-\lambda_{\mathrm{Bi}^{212}}t}$$

$$_{\mathrm{I}}S_{\mathrm{Bi}^{212}} = 2{\cdot}1 \times 10 - 2{\cdot}1 \times 10\,e^{-\lambda_{\mathrm{Bi}^{212}}t}$$

B. *Triple-track stars*

$$_{\mathrm{III}}S_{\mathrm{Ra}^{224}} = 2{\cdot}82 \times 10^2\,e^{-\lambda_{\mathrm{Ra}^{224}}t} - 2{\cdot}84 \times 10^2\,e^{-\lambda_{\mathrm{Pb}^{212}}t} + 2\,e^{-\lambda_{\mathrm{Bi}^{212}}}$$

C. *Quadruple-track stars*

$$_{\mathrm{IV}}S_{\mathrm{Ra}^{228}} = 3{\cdot}46 \times 10^2\,e^{-\lambda_{\mathrm{Ra}^{228}}t} - 3{\cdot}47 \times 10^2\,e^{-\lambda_{\mathrm{Th}^{228}}t} + 2\,e^{-\lambda_{\mathrm{Ra}^{224}}t}$$

$$_{\mathrm{IV}}S_{\mathrm{Th}^{228}} = 2{\cdot}49 \times 10^2\,e^{-\lambda_{\mathrm{Th}^{228}}t} - 2{\cdot}83 \times 10^2\,e^{-\lambda_{\mathrm{Ra}^{224}}t} + 3{\cdot}5 \times 10\,e^{-\lambda_{\mathrm{Pb}^{212}}t}$$

$$_{\mathrm{IV}}S_{\mathrm{Ra}^{224}} = 2{\cdot}84 \times 10^2\,e^{-\lambda_{\mathrm{Pb}^{212}}t} - 2{\cdot}14_2 \times 10^3\,e^{-\lambda_{\mathrm{Ra}^{224}}t} - 2\,e^{-\lambda_{\mathrm{Bi}^{212}}t} + 1{\cdot}860 \times 10^3$$

D. *Quintuple-track stars*

$$_{\mathrm{V}}S_{\mathrm{Th}^{232}} = 2{\cdot}47 \times 10^2\,e^{-\lambda_{\mathrm{Th}^{232}}t} - 3{\cdot}46 \times 10^2\,e^{-\lambda_{\mathrm{Ra}^{228}}t} + 9{\cdot}9 \times 10\,e^{-\lambda_{\mathrm{Th}^{228}}}$$

$$_{\mathrm{V}}S_{\mathrm{Ac}^{228}} = 1{\cdot}31 \times 10^2 - 1{\cdot}31 \times 10^2\,e^{-\lambda_{\mathrm{Th}^{228}}t} + 1\,e^{-\lambda_{\mathrm{Ra}^{224}}t}$$

$$_{\mathrm{V}}S_{\mathrm{Ra}^{228}} = 1{\cdot}2 \times 10 - 2{\cdot}6 \times 10^{-5}\,t + 2{\cdot}3_9 \times 10^{-11}\,t^2 - 1{\cdot}2 \times 10\,e^{-\lambda_{\mathrm{Ra}^{224}}t}$$

$$_{\mathrm{V}}S_{\mathrm{Th}^{228}} = 2{\cdot}15_4 \times 10^3\,e^{-\lambda_{\mathrm{Ra}^{224}}t} - 3{\cdot}5 \times 10\,e^{-\lambda_{\mathrm{Pb}^{212}}t} - 2{\cdot}11_9 \times 10^3 + 4{\cdot}12_5 \times 10^{-3}\,t - 2{\cdot}38_4 \times 10^{-11}\,t^2$$

II. Uranium^{238} series

A. *Single-track stars*

$$_{\mathrm{I}}S_{\mathrm{U}^{238}} = 1{\cdot}23_4 \times 10^{-2}\,t$$

$$_{\mathrm{I}}S_{\mathrm{U}^{234}} = 1{\cdot}23_5 \times 10^{-2}\,t$$

$$_{\mathrm{I}}S_{\mathrm{Th}^{230}} = 1{\cdot}23_5 \times 10^{-2}\,t$$

$$_{\mathrm{I}}S_{\mathrm{Ra}^{226}} = 5{\cdot}88_7 \times 10^3\,e^{-\lambda_{\mathrm{Ra}^{226}}t} - 5{\cdot}88_7 \times 10^3\,e^{-\lambda_{\mathrm{Rn}^{222}}t}$$

$$_{\mathrm{I}}S_{\mathrm{Pb}^{214}} = 7{\cdot}9 \times 10\,e^{-\lambda_{\mathrm{Bi}^{214}}t} - 1{\cdot}08 \times 10^2\,e^{-\lambda_{\mathrm{Pb}^{214}}t} + 2{\cdot}9 \times 10\,e^{-\lambda_{\mathrm{Pb}^{210}}t}$$

$$_{\mathrm{I}}S_{\mathrm{Bi}^{214}} = 2{\cdot}1 \times 10\,e^{-\lambda_{\mathrm{Pb}^{210}}t} - 2{\cdot}1 \times 10\,e^{-\lambda_{\mathrm{Bi}^{214}}t}$$

$$_{\mathrm{I}}S_{\mathrm{Bi}^{210}} = 2{\cdot}71 \times 10^2\,e^{-\lambda_{\mathrm{Bi}^{210}}t} - 7{\cdot}73_5 \times 10^3\,e^{-\lambda_{\mathrm{Po}^{210}}t} + 7{\cdot}464 \times 10^3$$

$$_{\mathrm{I}}S_{\mathrm{Pb}^{210}} = 2{\cdot}71 \times 10^2 - 4{\cdot}48_8 \times 10^{-4}\,t + 3{\cdot}71_1 \times 10^{-10}\,t^2 - 7{\cdot}290 \times 10^{-18}\,t^3 - 2{\cdot}71 \times 10^2\,e^{-\lambda_{\mathrm{Bi}^{210}}t}$$

$$_{\mathrm{I}}S_{\mathrm{Po}^{210}} = 1{\cdot}23_5 \times 10^{-2}\,t - 3{\cdot}57_9 \times 10^{-10}\,t^2 + 6{\cdot}91_6 \times 10^{-18}\,t^3$$

Table 1 (*continued*)

B. *Double-track stars*

$$_{II}S_{Ra^{226}} = 3\,e^{-\lambda_{Ra^{226}}t} - 3\,e^{-\lambda_{Rn^{222}}t}$$

$$_{II}S_{Rn^{222}} = 5{\cdot}0 \times 10\,e^{-\lambda_{Rn^{222}}t} + 3\,e^{-\lambda_{Po^{218}}t} - 1{\cdot}23 \times 10\,e^{-\lambda_{Pb^{214}}t} + 6{\cdot}9 \times 10\,e^{-\lambda_{Bi^{214}}t}$$

$$_{II}S_{Po^{218}} = 1{\cdot}1 \times 10\,e^{-\lambda_{Bi^{214}}t} + 3\,e^{-\lambda_{Pb^{210}}t} - 1{\cdot}4 \times 10\,e^{-\lambda_{Pb^{214}}t}$$

C. *Triple-track stars*

$$_{III}S_{Ra^{226}} = 5{\cdot}0 \times 10\,e^{-\lambda_{Ra^{226}}t} - 5{\cdot}0 \times 10\,e^{-\lambda_{Rn^{222}}t} + 1\,e^{-\lambda_{Pb^{214}}t}$$

$$_{III}S_{Rn^{222}} = 1{\cdot}23 \times 10^2\,e^{-\lambda_{Pb^{214}}t} - 5{\cdot}94_3 \times 10^3\,e^{-\lambda_{Rn^{222}}t} - 6{\cdot}9 \times 10\,e^{-\lambda_{Bi^{214}}} + 5{\cdot}89_0 \times 10^3\,e^{-\lambda_{Pb^{210}}t}$$

D. *Quadruple-track stars*

$$_{IV}S_{Ra^{226}} = 5{\cdot}94_3 \times 10^3\,e^{-\lambda_{Rn^{222}}t} - 5{\cdot}94_3 \times 10^3 + 1{\cdot}23_5 \times 10^{-2}\,t + 6{\cdot}24_9 \times 10^{-12}\,t^2$$

III. Uranium^{235} series

A. *Single-track stars*

$$_{I}S_{U^{235}} = 5{\cdot}67_8 \times 10^{-4}\,t$$

$$_{I}S_{Pa^{231}} = 5{\cdot}69_1 \times 10^{-4}\,t - 3 + 3\,e^{-\lambda_{Th^{227}}}$$

$$_{I}S_{Ac^{227}} = 1{\cdot}20_9 \times 10^{-10}\,t^2 - 4{\cdot}63_2 \times 10^{-17}\,t^3 + 1{\cdot}01_7 \times 10^{-23}\,t^4 - 1{\cdot}61_9 \times 10^{-30}\,t^5 + 2{\cdot}05_0 \times 10^{-37}\,t^6 - 2{\cdot}17_0 \times 10^{-44}\,t^7 + 1{\cdot}0 \times 10\,e^{-\lambda_{Ac^{227}}t} - 1{\cdot}0 \times 10\,e^{-\lambda_{Ra^{223}}t}$$

$$_{I}S_{Th^{227}} = 5{\cdot}60_9 \times 10^{-4}\,t - 3{\cdot}21_9 \times 10^{-10}t^2 + 9{\cdot}42_4 \times 10^{-17}\,t^3 - 1{\cdot}87_6 \times 10^{-23}\,t^4 + 2{\cdot}84_8 \times 10^{-30}\,t^5 - 3{\cdot}51_7 \times 10^{-37}\,t^6 + 3{\cdot}67_1 \times 10^{-44}\,t^7$$

$$_{I}S_{Pb^{211}} = 2 - 2\,e^{-\lambda_{Pb^{211}}t}$$

B. *Quadruple-track stars*

$$_{IV}S_{Ac^{227}} = 2\,e^{-\lambda_{Ac^{227}}t} + 3\,e^{-\lambda_{Ra^{223}}t} - 5\,e^{-\lambda_{Th^{227}}t}$$

$$_{IV}S_{Th^{227}} = 5\,e^{-\lambda_{Th^{227}}t} - 5\,e^{-\lambda_{Ra^{223}}t}$$

$$_{IV}S_{Ra^{223}} = 5{\cdot}67_5 \times 10^{-4}\,t - 2{\cdot}03_2 \times 10^{-10}\,t^2 + 4{\cdot}85_3 \times 10^{-17}\,t^3 - 8{\cdot}69_1 \times 10^{-24}\,t^4 + 1{\cdot}24_5 \times 10^{-30}\,t^5 - 1{\cdot}48_6 \times 10^{-37}\,t^6 + 1{\cdot}52_1 \times 10^{-44}\,t^7 + 2\,e^{-\lambda_{Pb^{211}}t} - 2\,e^{-\lambda_{Ra^{223}}t}$$

C. *Quintuple-track stars*

$$_{V}S_{Ac^{227}} = 8{\cdot}60_4 \times 10^{-6}\,t - 4{\cdot}75_5 \times 10^{-13}\,t^2 + 2{\cdot}89_2 \times 10^{-17}\,t^3 - 8{\cdot}29_5 \times 10^{-24}\,t^4 + 1{\cdot}45_7 \times 10^{-30}\,t^5 - 1{\cdot}93_3 \times 10^{-37}\,t^6 + 2{\cdot}09_7 \times 10^{-44}\,t^7 - 1{\cdot}6 \times 10 + 1{\cdot}0 \times 10\,e^{-\lambda_{Th^{227}}t} + 6\,e^{-\lambda_{Ra^{223}}t}$$

$$_{V}S_{Th^{227}} = 4 - 1{\cdot}50_4 \times 10^{-6}\,t + 2{\cdot}01_2 \times 10^{-10}\,t^2 - 7{\cdot}68_3 \times 10^{-17}\,t^3 + 1{\cdot}68_7 \times 10^{-23}\,t^4 - 2{\cdot}68_5 \times 10^{-30}\,t^5 + 3{\cdot}39_9 \times 10^{-37}\,t^6 - 3{\cdot}59_6 \times 10^{-44}\,t^7 - 1{\cdot}0 \times 10\,e^{-\lambda_{Th^{227}}t} + 6\,e^{-\lambda_{Ra^{223}}t}$$

Table 2. Summation formulae for each series

I. Thorium^{232} series

$$_{I}S = 4{\cdot}07_8 \times 10^{-3}\,t + 2{\cdot}60_1 \times 10^{3}\,e^{-\lambda_{Ra^{228}}t} - 2{\cdot}61_1 \times 10^{3}\,e^{-\lambda_{Th^{228}}t} - 1{\cdot}85_9 \times 10^{3}\,e^{-\lambda_{Ra^{224}}t} + 2{\cdot}11_7 \times 10^{3} \times 2{\cdot}51 \times 10^{2}\,e^{-\lambda_{Pb^{212}}t} + 4\,e^{-\lambda_{Bi^{212}}t}$$

$$_{III}S = 2{\cdot}82 \times 10^{2}\,e^{-\lambda_{Ra^{224}}t} - 2{\cdot}84 \times 10^{2}\,e^{-\lambda_{Pb^{212}}t} + 2\,e^{-\lambda_{Bi^{212}}t}$$

$$_{IV}S = 3{\cdot}46 \times 10^{2}\,e^{-\lambda_{Ra^{228}}t} - 9{\cdot}9 \times 10\,e^{-\lambda_{Th^{228}}t} - 2{\cdot}42_4 \times 10^{3}\,e^{-\lambda_{Ra^{224}}t} + 3{\cdot}19 \times 10^{2}\,e^{-\lambda_{Pb^{212}}t} - 2\,e^{-\lambda_{Bi^{212}}t} + 1{\cdot}860 \times 10^{3}$$

$$_{V}S = 2{\cdot}47 \times 10^{2}\,e^{-\lambda_{Th^{232}}t} - 3{\cdot}46 \times 10^{2}\,e^{-\lambda_{Ra^{228}}t} - 3{\cdot}3 \times 10\,e^{-\lambda_{Th^{228}}t} - 1{\cdot}97_6 \times 10^{3} + 2{\cdot}14_3 \times 10^{3}\,e^{-\lambda_{Ra^{224}}t} - 3{\cdot}5 \times 10\,e^{-\lambda_{Pb^{212}}t} + 4{\cdot}09_9 \times 10^{-3}\,t$$

II. Uranium^{238} series

$$_{I}S = 7{\cdot}73_5 \times 10^{3} + 4{\cdot}89_4 \times 10^{-2}\,t + 1{\cdot}32 \times 10^{-11}\,t^2 - 3{\cdot}74 \times 10^{-19}\,t^3 + 5{\cdot}88_7 \times 10^{3}\,e^{-\lambda_{Ra^{226}}t} - 5{\cdot}88_7 \times 10^{3}\,e^{-\lambda_{Rn^{222}}t} - 1{\cdot}08 \times 10^{2}\,e^{-\lambda_{Pb^{214}}t} + 5{\cdot}8 \times 10\,e^{-\lambda_{Bi^{214}}t} + 5{\cdot}0 \times 10\,e^{-\lambda_{Pb^{210}}t} - 7{\cdot}73_5 \times 10^{3}\,e^{-\lambda_{Po^{210}}t}$$

$$_{II}S = 3\,e^{-\lambda_{Ra^{226}}t} + 4{\cdot}7 \times 10\,e^{-\lambda_{Rn^{222}}t} + 3\,e^{-\lambda_{Po^{218}}t} - 1{\cdot}37 \times 10^{2}\,e^{-\lambda_{Pb^{214}}t} + 8{\cdot}0 \times 10\,e^{-\lambda_{Bi^{214}}t} + 3\,e^{-\lambda_{Pb^{210}}t}$$

$$_{III}S = 5{\cdot}0 \times 10\,e^{-\lambda_{Ra^{226}}t} - 5{\cdot}99_3 \times 10^{3}\,e^{-\lambda_{Rn^{222}}t} + 1{\cdot}23 \times 10^{2}\,e^{-\lambda_{Pb^{214}}t} - 7{\cdot}0 \times 10\,e^{-\lambda_{Bi^{214}}t} + 5{\cdot}890 \times 10^{3}\,e^{-\lambda_{Pb^{210}}t}$$

$$_{IV}S = -5{\cdot}94_3 \times 10^{3}\,e^{-\lambda_{Rn^{222}}t} - 5{\cdot}94_3 \times 10^{3} + 1{\cdot}23_5 \times 10^{-2}\,t + 6{\cdot}24_9 \times 10^{-12}\,t^2$$

III. Uranium^{235} series

$$_{I}S = 1{\cdot}69_8 \times 10^{-3}\,t - 2{\cdot}01_2 \times 10^{-10}\,t^2 + 4{\cdot}79_1 \times 10^{-17}\,t^3 - 8{\cdot}58_3 \times 10^{-24}\,t^4 + 1{\cdot}22_9 \times 10^{-3}\,t^5 - 1{\cdot}46_6 \times 10^{-37}\,t^6 + 1{\cdot}50_1 \times 10^{-44}\,t^7 - 1 + 3\,e^{-\lambda_{Th^{227}}t} + 1{\cdot}0 \times 10\,e^{-\lambda_{Ac^{227}}t} - 1{\cdot}0 \times 10\,e^{-\lambda_{Ra^{223}}t} - 2\,e^{-\lambda_{Pb^{211}}t}$$

$$_{IV}S = 5{\cdot}67_5 \times 10^{-4}\,t - 2{\cdot}03_2 \times 10^{-10}\,t^2 + 4{\cdot}85_3 \times 10^{-17}\,t^3 - 8{\cdot}69_1 \times 10^{-24}\,t^4 + 1{\cdot}24_5 \times 10^{-30}\,t^5 - 1{\cdot}48_6 \times 10^{-37}\,t^6 + 1{\cdot}52_1 \times 10^{-44}\,t^7 - 4\,e^{-\lambda_{Ra^{223}}t} + 2\,e^{-\lambda_{Pb^{211}}t} + 2\,e^{-\lambda_{Ac^{227}}t}$$

$$_{V}S = 7{\cdot}10 \times 10^{-6}\,t + 2{\cdot}00_6 \times 10^{-10}\,t^2 - 4{\cdot}79 \times 10^{-17}\,t^3 + 8{\cdot}57_6 \times 10^{-24}\,t^4 - 1{\cdot}22_8 \times 10^{-30}\,t^5 + 1{\cdot}46_5 \times 10^{-37}\,t^6 - 1{\cdot}49_9 \times 10^{-44}\,t^7 - 1{\cdot}2 \times 10 + 1{\cdot}2 \times 10\,e^{-\lambda_{Ra^{223}}t}$$

Discussion

Flamant (1948) has calculated the probability of existence of multiple-track stars in a series in equilibrium relative to the number of disintegrations of the parent nuclide of the series. For daughter elements with relatively long half-lives the number of disintegrations of the amount originally present is essentially the same as the number for the parent nuclide of the series. Thus, Flamant's probabilities give the percentage star type distribution for long half-lived isolated emitters as well as for the entire series in equilibrium. A comparison of Flamant's method and our method is shown in Table 3 for the long half-lived emitter Th^{228}.

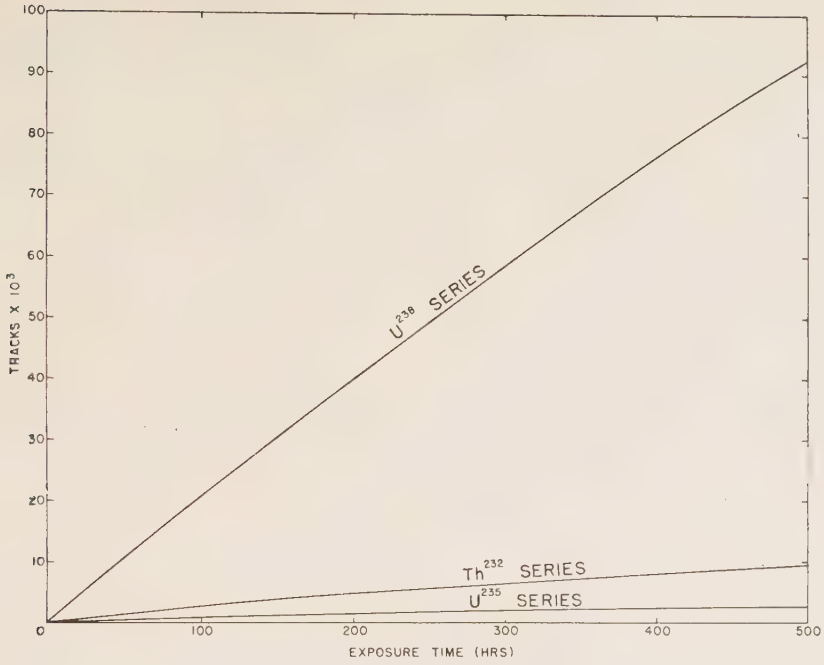

Fig. 2. Total single-track star population versus time for one microgram of thorium or uranium in equilibrium with their daughter products.

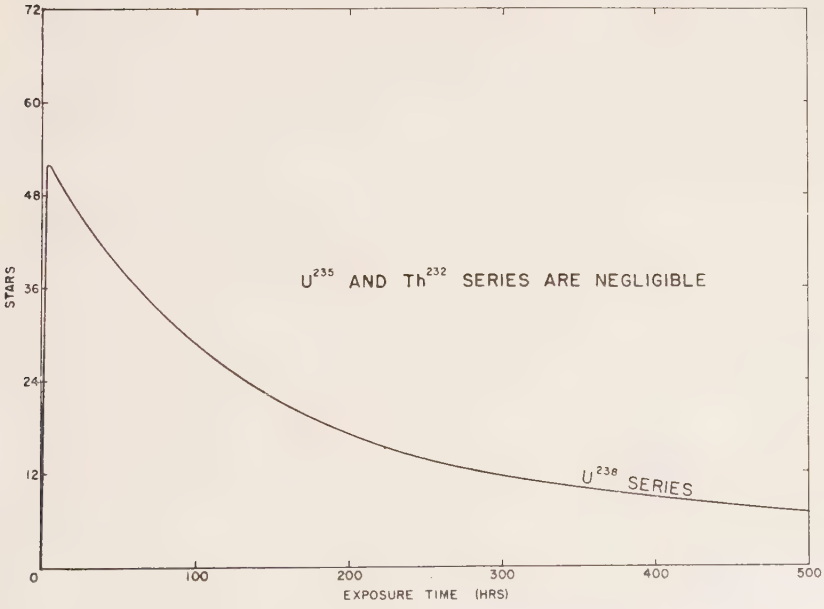

Fig. 3. Total double-track star population versus time for one microgram of thorium or uranium in equilibrium with their daughter products.

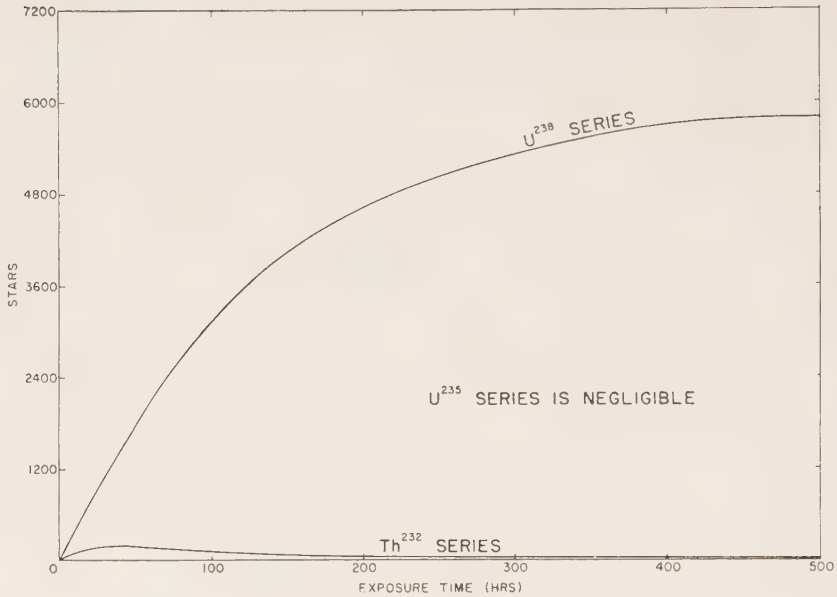

Fig. 4. Total triple-track star population versus time for one microgram of thorium or uranium in equilibrium with their daughter products.

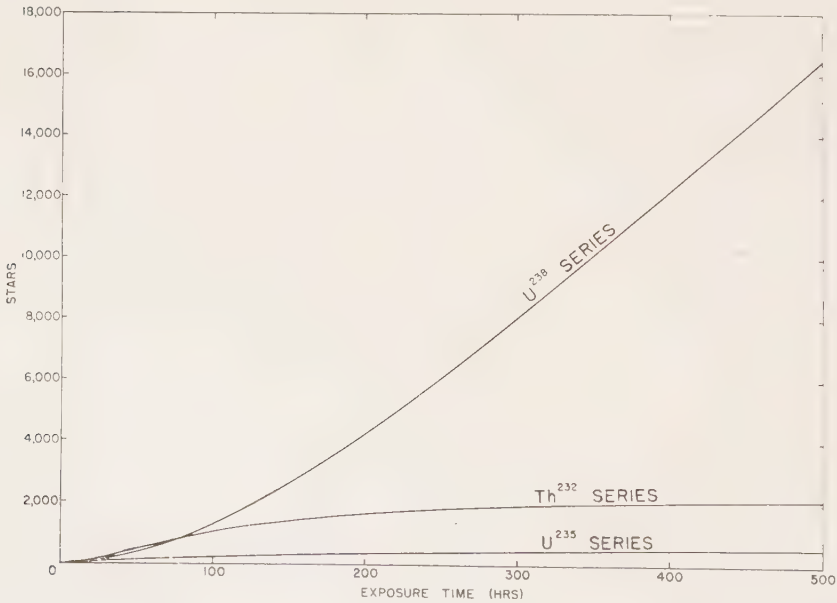

Fig. 5. Total quadruple-track star population versus time for one microgram of thorium or uranium in equilibrium with their daughter products.

For the short half-lived daughter elements, however, the number of disintegrations of the atoms originally present during the exposure time is less than the number of disintegrations of the parent nuclide. The number of disintegrations must be calculated relative to the number of disintegrations of the atoms originally present. The formulae in Table 1 enable one to calculate the percentage star type distribution for isolated emitters regardless of the length of the half-life.

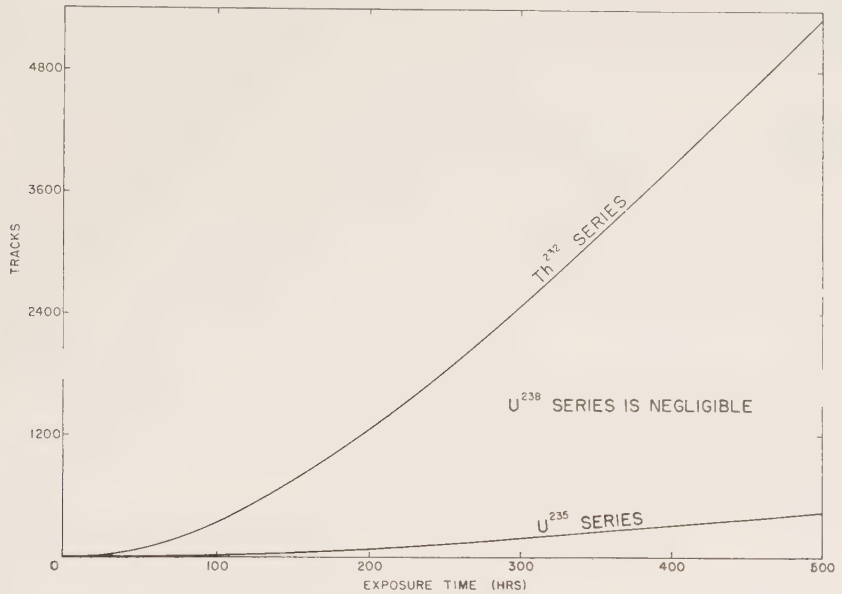

Fig. 6. Total quintuple-track star population versus time for one microgram of thorium or uranium in equilibrium with their daughter products.

Star splitting due to diffusion in the uranium series has been investigated by Frota-Pessôa and in the thorium series by Eichholz and Flack (1951). In both cases the effect of star splitting was observed at room temperatures and for analytical work could probably be minimized by exposing the plates at lower temperatures (Picciotto, personal communication).

Table 3. *Comparison of* Th^{228} *star populations determined by* Flamant (1948) *and by the method presented here*

Track type	*Emitter in equilibrium* (Flamant, 1948) *in percent*	*Isolated emitter* (*this paper*) *in percent*
Single tracks	25	25
Quadruple tracks	2	3
Quintuple tracks (via Po^{212})	25	72
Quintuple tracks (via Tl^{208})	48	

Analytical Applications

The theoretical calculations reported in this paper were undertaken in an effort to develop a method of thorium analysis for less than microgram amounts in the presence of larger amounts of uranium. The quantitative analysis of thorium by determining the abundance of five-branched stars in a loaded nuclear emulsion and the comparison of observed and predicted star populations in loaded emulsions will be presented in a separate paper. The comparison of observed and predicted star populations may also be used to check the half-lives of several members of the uranium and thorium series. Variations in the star populations with depth in the emulsion and splitting of stars may be used to study rates of diffusion in the emulsions of the different members of the radioactive series.

As the uranium analysis can be readily made by conventional chemical methods, the following proposed star-counting technique can be used for thorium analysis in low concentrations. To the solution of a sample containing uranium and thorium which has been stripped of its radium and radon, but whose specific beta activity is known, add a known amount of Th^{234} (as a radiotracer for Th^{228}). A nuclear emulsion is then loaded by immersion in the resulting solution, dried, and the beta activity per unit area of the emulsion is measured. The volume of solution per unit area taken up by the emulsion is determined by its beta activity. After suitable exposure, the loaded emulsion is developed and the number of five-branched stars per unit area is determined. The number of five-branched stars counted can be corrected by subtracting the five-branched stars produced by the Ra^{223} in the U^{235} series as the total uranium concentration is known. For a given exposure the number of micrograms of thorium in the original solution is equal to

$$\text{Th (micrograms/ml)} = \frac{A}{{}_V S_{\text{Th}^{228}}} \left[N - \frac{0.00715 U \cdot {}_V S_{\text{U}^{235}}}{A} \right]$$

where A is the loading factor in cm^2/ml, N is the number of five-branched stars per unit area counted, and U is the uranium concentration in micrograms/ml.

If a nuclear emulsion is loaded with a solution of uranium and thorium in equilibrium, the thorium content of the solution can be determined using a method of simultaneous equations similar to that discussed by Schneider and Matitsch. This method is useful for the Th/U ratios in the range from 0·01 to 1·0.

If Q_1 and Q_2 are the track counts of two different exposure times, then the following equations will hold for the thorium and uranium content of a given volume of the emulsion

$$Q_1 = k_1 \,\text{Th} + k_2 \, U, \text{ for } t = t_1$$

$$Q_2 = k_3 \,\text{Th} + k_4 \, U, \text{ for } t = t_2$$

The k constants are the number of five-track stars per atom of the parent element. They may be calculated by evaluating the series formula for the respective times and dividing by the number of atoms of parent nuclide in one microgram. This

$$k_1, k_3 = \frac{S_{\text{Th}}}{2{\cdot}59 \times 10^{15}}; \qquad k_2, k_4 = \frac{S_{\text{U}^{235}}}{2{\cdot}53 \times 10^{15}}$$

The Th/U atom ratio obtained from the above equations must be multiplied by the ratio of atomic weights in order to convert the atom ratio to a weight ratio. Uranium, determined by a conventional analysis, can then be inserted into this ratio to determine the thorium content.

The authors wish to thank F. J. Flanagan and Barbara Schwartz for their assistance in making the calculations. This work is part of a programme undertaken by the U.S. Geological Survey on behalf of the Division of Raw Materials of the Atomic Energy Commission.

References

Bateman, H. (1910) The solution of a system of differential equations occurring in the theory of radioactive transformations. Cambridge Phil. Soc. Proc. **15,** 423–427

Eichholz, G. G., and Flack, F. C. (1951) The diffusion of thoron atoms through photographic gelatin. J. Phys. Chem. **19,** 363–660

Flamant, R. (1948) Sur la probabilite de formation d'etoiles de desintegrations successives dans les emulsions photographiques. Univ. Bruxelles, Centre Physique Nucleaire Bull. 3

Flanagan, F. J., and Senftle, F. E. (1954) Tables for evaluating Bateman's equation coefficients for radioactivity calculations. (In preparation)

Frota-Pessôa, Elisa (1952) Note on the diffusion of radioelements in nuclear emulsion. Centro Brasileiro des Pesquisas Fisicas, Notas de Fisica No. 11

Issac, N., and Picciotto, E. (1953) Ionium determination in deep-sea sediments. Nature **171,** No. 4356, 742–743

Schneider, W., and Matitsch, T. (1952) Eine Photographische Methode zur quantitativen Bestimmung von Actinium. Sitzungsberichte **161,** Abt. IIa, 131–150

Yagoda, Herman (1949) Radioactive Measurements with Nuclear Emulsions. New York, John Wiley and Sons

---

Book review

Catalogue of Meteorites with special reference to those represented in the collection of the British Museum (Natural History). By G. T. Prior; second, revised, and enlarged edition by Max H. Hey. (London, British Museum, 1953). £3 10s.

The "Catalogue of Meteorites" published in 1923 by the Keeper of the Mineral Department of the British Museum, Dr. G. T. Prior, was written to fulfil a double purpose, to provide a Guide to the large meteorite collection under his care, and to present a complete list of all the meteorites known. It was very useful in both respects; the great care with which it had been compiled, made it a most reliable source of information which was consulted all over the world. In 1927 a small appendix was provided by Dr. Prior, and in 1940 a larger one by Dr. Max H. Hey. Now an entirely new edition of the Catalogue has been issued by Dr. Hey; this not only saves us the trouble of having to look for each meteorite in three different places, but brings the whole subject up to date. The book is now largely the work of the second editor, and although his share is correctly mentioned on the title page, on the back of the binding his name is missing—a slight but regrettable oversight which can probably still be corrected for a part of the edition.

To characterize the new edition it is sufficient to say that it shows all the merits of Prior's classical work: greatest reliability of the data, a very concise text, packed with information, and clear printing. The chapter on meteorite craters, from the second appendix, has been greatly

enlarged; as some of these craters are of doubtful origin, the author had no easy task in dealing critically with the various claims. Tektites, the glass pieces whose meteoritic origin is in the opinion of some authorities not yet proven beyond any possible doubt, are even in the preface not mentioned with a single word, although the British Museum has a good collection of them. A very welcome addition are the longitude and latitude data now given for each fall and find; most of those interested in the exact place on our Earth where a meteorite has come to rest will probably agree that this simplest and well-known method of indicating the geographical position is preferable to the introduction of the "co-ordinate numbers" recommended by some "meteoriticists."

Concerning the nomenclature of meteorites, the principles which have been followed are stated in the preface. "Unnecessary changes of names are to be deprecated, as liable to cause confusion." Surely once a certain place name has been generally accepted as the nearest one to a meteorite fall or find, it is not worth while altering it, even if the modern spelling of the name should be different, or if renewed researches have proved a slight geographical error. We are only interested in a stable and universally accepted nomenclature of the specimens, and the rule to look for the nearest place name is nothing but a help to this effect, not a scientifically important aim in itself. We are, therefore, rather astonished to see that the name "Bethany," used in the previous three publications of the British Museum as the general name for the many African meteorites which have been found in a restricted area and are, perhaps, parts of one shower, has now been replaced by "Gibeon"; this seems just an instance of an unnecessary and unwelcome alteration, so rightly discouraged in the preface.

As a recommendation for a future edition we should like to express the wish that the same meticulous care which is devoted to the choice of place names should also be extended to the names of persons. We have noticed the perpetuation of a mistake which has been exposed years ago; the well-known etchings on iron meteorites are constantly called WIDMANSTETTER, instead of, as usual, WIDMANSTÄTTEN, figures. This is certainly due to the fact that a Keeper of the British Museum once discovered that the form WIDMANSTETTER had been used by an Austrian family and, unaware of the variability of family names in earlier days, concluded that this must be the authentic form. However, immediate researches in Vienna and Graz left no doubt that the discoverer of the etching figures himself actually wrote WIDMANSTÄTTEN and was under this name known to the authorities and his friends; so that, in the words of the investigator Professor STEFAN MEYER, it would be a "historical falsification" to change it (see Popular Astronomy **46**, 469, 1938). Even if the WIDMANSTETTERS had been ALOYS VON WIDMANSTÄTTEN'S real forefathers—the relationship is more complicated—we could not now deny him the right of a spelling different from other members of the family. Alternatively, for the sake of consistency, at least one more famous name which appears frequently in the Catalogue would have to be altered; instead of CHLADNI the Catalogue would have to say CHLADENIUS, because this is the form E. F. F. CHLADNI'S father and grandfather had used!

Considering the excellency of the typographical production, the price of £3. 10s. cannot be considered as too high.

F. A. PANETH

INFORMATION FOR CONTRIBUTORS

I. GENERAL

1. Papers on Geochemistry should be submitted to the editors for the appropriate country or language (*Papers on Cosmochemistry should be sent to Prof. F. A. Paneth, F.R.S.*). Papers submitted for publication will naturally be judged from the standpoint of scientific originality and novelty. Technical details of apparatus used in scientific investigation can, however, be presented in brief notes. The preparation of progress reports and review articles will be invited by the Editors from time to time. The Journal will appear as independent and complete numbers, which will be sold separately and combined into volumes of about 300 pages.

2. Only papers which have not been previously published will be accepted. The publishers retain exclusive publication rights for all papers in all languages and countries, on acceptance and until the 31st December of the year following the year when the printed paper appears. Authors must agree not to publish elsewhere a paper submitted to and accepted by *Geochimica et Cosmochimica Acta.*

3. Authors will receive 75 free reprints of their papers. Additional copies can be purchased if ordered at the time the first proofs are returned.

II. MANUSCRIPT REQUIREMENTS

1. The manuscript must be written in one of the three official languages, English, French, or German.

2. The manuscript should be an original typewritten copy (not a carbon). The text must be ready for printing and should be carefully checked for errors. Authors will receive proofs for correction.

3. Half-tone illustrations are to be restricted to the minimum necessary. They should accompany the manuscript mounted on separate sheets. Line drawings may be redrawn for the sake of uniformity and should therefore include all relevant details. Photographs should be enlarged sufficiently to permit their clear reproduction in half-tone. If words or numbers appear in photographs, two copies are requested, one clearly printed and the other without inscription. All illustrations should be provided with descriptive legends, which should accompany the manuscript on a separate sheet.

4. Only such references to literature should be given as are referred to in the text. Literature references are to be listed together at the end of the manuscript and not given as footnotes. **All references should be listed alphabetically according to the Harvard system :**

AHRENS, L. H. (1952) *Geochim. et Cosmochim. Acta*, 2, 168.

and should include the standard abbreviated title of the journal, year, volume number and page number.

5. The text of articles submitted should be concise and in a readily understandable style. The technical description of the methods used should only be given in detail when such methods are new. The essential contents of each paper should be briefly recapitulated in an abstract in English. Such an abstract may, however, be submitted by the author in the language of the original typescript for translation into English by the editorial staff.

6. To conserve space authors are requested to mark less important portions of the paper (such as description of methods, record of experimental results, etc.) for printing in smaller type

D IN STACKS

PERGAMON PRESS LTD

Books of interest to readers of this journal

COALS AND BITUMENS and related fossil carbonaceous substances
By S. I. TOMKEIEFF, D.Sc., F.R.S.E. 126 *pp.* 4 *illus.* 17*s.* 6*d. net*

QUANTITATIVE SPECTROCHEMICAL ANALYSIS OF SILICATES
By L. H. AHRENS, D.Sc., F.R.I.C. 120 *pp.* 35 *illus.* 25*s. net*

ISOTOPE GEOLOGY
By KALERVO RANKAMA, Ph.D. 552 *pp.* 41 *illus.* 75*s. net*
(Distributed in the Western Hemisphere by the McGraw-Hill Book Co., Inc.)

Prospectuses are available on request

Vol. 2, No. 1, just published

DEEP-SEA RESEARCH

A QUARTERLY RESEARCH JOURNAL

Edited by
PROF. L. FAGE C. D. OVEY, B.Sc., M.A. DR. MARY SEARS

CONTENTS

FRED B. PHLEGER: Foraminifera and deep-sea research.

CLAUDE E. ZOBELL: Some effects of high hydrostatic pressure on apparatus observed on the Danish Galathea Deep-Sea expedition.

K. F. BOWDEN: The direct measurements of subsurface currents in the oceans.

ROBERT L. FISHER: On sounding of trenches.

DAYTON E. CARRITT: Atmospheric pressure changes and gas solubility.

R. B. MONTGOMERY and WARREN S. WOOSTER: Thermostatic anomaly and the analysis of serial oceanographic data.

PAUL FERRIS SMITH: Further measurements of the sound scattering properties of several marine organisms.

G. P. D. HALL: Survey of newly discovered feature (Genista Bank) off the Arabian Coast.

ANTON FR. BRUUN: An oceanographic organisation for the Indo-Pacific region.

ANTON FR. BRUUN: Oceanography at the Eighth Pacific Science Congress.

Price per volume (4 issues) £4 10*s.* ($12.60)

242 MARYLEBONE ROAD · LONDON N·W·1

PRINTED AT THE PITMAN PRESS, BELFAST